

Metasomatism and metasomatic rocks

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Abstract

This book describes the main types of metasomatic processes and outlines the theoretical bases of metasomatism in accordance with the theory of D. S. Korzhinsky. Thermodynamics, dynamics and ideas concerning self-organisation of metasomatic processes are developed according to the current theoretical level. Results are given concerning technics of experimental study of metasomatism. The relation of metasomatism to ore deposits is discussed, and the new concept of formation of ore-concentrating dense salt melts and related light metasomatic fluids is proposed. The significant part of the monograph contains the characteristics of the main metasomatic families and rocks. Detailed characteristics of geological setting, mineral composition, facies and genetical considerations are given based on original and literature data.

This book may be interesting for petrologists, geologists studying ore deposits and specialists in metasomatism. It can be used as a textbook of metasomatism for graduate and postgraduate students.

22 tables, 127 figures, 462 bibliographic references.

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Key-words : metasomatism ; metasomatic processes ; metasomatic rocks ; Korzhinskii ; ore deposits ; self-organisation ; thermodynamics ; chemical kinetics ; experimentation ; skarns ; greisens ; propylites ; secondary quartzites ; beresites ; alkaline metasomatic rocks ; gumbelites ; argillites

Foreword to the English translation

The text presented here was published in Russian in 1998 by World Scientific Moscow under the aegis of the Russian Academy of Sciences (ISBN 5-891 176 -038- X). It was translated into English by Jean Verkaeren (Honorary Professor, University of Louvain-la-Neuve, Belgium) and Jacques Duchesne (Honorary Professor, University of Liège, Belgium) during the period 2000-2010, assisted by Bernard Guy on some points (the English translation was prepared in parallel with, and after, the first French translation). The edition of this file has been made by Bernard Guy (Director of Research at the Ecole Nationale Supérieure des Mines de Saint-Etienne) in 2014-2015. During a trip to Moscow in 2003, Jean Verkaeren and Bernard Guy met the authors of the book, discussed some technical issues, and received permission to develop this translation and make it accessible to English- and French- speaking scientific communities. The presentation has been simplified by grouping the figures at the end of each chapter. All figure symbols have not been translated into French nor English: in this English edition, symbols in Russian, or even French (as remains of the first translation step) may be found. We temporarily leave things as they are, in order to avoid further delay in the presentation of the book. Similarly the table of contents is given with no indication of the page numbers. Corrections to the translation and improvements of the presentation will be made in later versions. Thank you to readers to report any problems they might identify in this edition (guy@emse.fr).

References: References appear in three groups: - the English translations of the Russian references (alphabetic order following the Latin characters) ; - the French translation of the Russian references, together with the original Russian references (alphabetic order following the Latin characters); - the general western (latin characters), non-Russian, references (mostly English).

Some articles published in Russian have been translated into English journals such as Geochemistry International, Geological Review, etc., to which the reader may refer.

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Symbols of minerals

Ab	—	albite
Acm	—	acmite
Act	—	actinolite
Ad	—	adularia
Adr	—	andradite
Aeg	—	aegyrine
Ak	—	akermanite
Alun	—	alunite
Amph	—	amphibole
An	—	anorthite
Anc	—	analcime
Ank	—	ankerite
And	—	andalusite
Ap	—	apatite
Arf	—	arfvedsonite
Astr	—	astrophyllite
Bi	—	biotite
Brc	—	brucite
Brt	—	berthierite
Carb	—	carbonate
Cas	—	cassiterite
Cc	—	calcite
Ccn	—	cancrinite
Chl	—	chlorite
Chr	—	chromite
Chu	—	clinohumite
Cli	—	clintonite
Cor	—	cordierite
Cpx	—	clinopyroxene
Crn	—	corundum
Di	—	diopside
Dol	—	dolomite
Dsp	—	diaspore
En	—	enstatite
Ep	—	epidote

Fa	—	fayalite
Fl	—	fluorite
Fll	—	fluellite
Fo	—	forsterite
Fsp	—	feldspar
Fspd	—	feldspathoid
Gel	—	gehlenite
Gib	—	gibbsite
Grs	—	grossularite
Grt	—	garnet
Hbl	—	hornblend
Hd	—	hedenbergite
Hem	—	hematite
H-Mel	—	hydromelilite (cyanite et cebollite)
H-Mic	—	hydromica
Ill	—	illite
Kln	—	kaolinite
Kfs	—	K-feldspar
Ky	—	cyanite
Lf	—	leucophyllite
Lib	—	liebenerite
Ln	—	larnite
Ls	—	leucoxene
Mc	—	microcline
Me	—	meionite
Mel	—	melinite
Er	—	merwinite
Mgs	—	magnesite
Mic	—	mica
Mic-Mnt	—	mica-montmorillonite
Mlb	—	molybdenite
Mln	—	melanite
Mnt	—	montmorillonite
Ms	—	muscovite
Mt	—	magnetite
Mtc	—	monticellite
Nar	—	narsasukite
Ne	—	nepheline
Ol	—	olivine
Olg	—	oligoclase

Opx	—	orthopyroxene
Or	—	orthose
Per	—	periclase
Phl	—	phlogopite
Phn	—	phengite
Pl	—	plagioclase
Pmp	—	pumpellyite
Po	—	pyrrhotine
Prg	—	pargasite
Prh	—	prehnite
Prl	—	pyrophyllite
Prv	—	perovskite
Px	—	pyroxene
Py	—	pyrite
Qtz	—	quartz
Ran	—	rankinite
Rbk	—	riebeckite
Ru	—	rutile
Scp	—	scapolite
Sell	—	sellaite
Ser	—	sericite
Sil	—	sillimanite
Sod	—	sodalite
Spl	—	spinelle
Spn	—	sphene
Spur	—	spurrite
Srp	—	serpentine
TfBi	—	tetraferribiotite
Tfphl	—	tetraferriphlogopite
Ti-Mt	—	titanomagnetite
Tlc	—	talc
Toz	—	topaze
Tr	—	tremolite
Tu	—	tourmaline
Wes	—	vesuvianite
Wlf	—	wolframite
Wo	—	wollastonite
Zeol	—	zeolite
Zo	—	zoisite

Foreword

D.S. Korzhinsky published more than 40 years ago “Essay on the metasomatic processes”, in which he put forward, in a general and accessible form, the main new ideas about metasomatism, outlining its links with magmatism and metallogenesis, briefly characterizing the main types of metasomatic processes and their mutual relations. Simply and intelligibly written, the “Essay” in its foundation had profound theoretical elaborations of the problems [Korzhinsky 1951_{1,2}, 1952_{1,2}, 1953₂] and detailed monographic researches on metasomatites [Korzhinsky, 1947, 1948].

His “Essay on the metasomatic processes” greatly influenced in Russia the development of research on that subject. Many articles were published and the subject aroused great enthusiasm in international meetings of the Union, the first one in 1963 [Metasomatic changes in lateral rocks and their role in metallogenesis, 1966], the second in 1966 [Metasomatic problems, 1970], the third in 1976 [Metasomatoses and Metallogenesis, 1974], the fourth in 1976 [Metasomatoses and Metallogenesis, 1978], the fifth in 1982 [Metasomatoses and Metallogenesis, 1982]. The sixth [1987] dealt with metasomatic phenomena in pre-cambrian rock masses [Pre-cambrian metasomatites and their ore-genesis, 1989; Metasomatic processes in pre-cambrian rock masses, 1991]. Regional meetings took place in Ukraine, Kirgizstan, Ural and the Far East.

However, in the majority of articles published in proceedings of meetings and pages of other journals, description and interpretation of metasomatoses followed traditional presentations.

The main ideas developed between 1960 and 1990 were undoubtedly the study of metasomatites with new methodical positions, i.e. D.S.Korzhinsky’s theory of metasomatic zoning.

Corresponding articles try to get more and more room in the proceedings of conferences and in the pages of journals. Monographies appear where on the example of various metasomatic formations D.S.Korzhinsky’s theory of metasomatism is given concrete expression and is developed. Among the most brilliant are “Geology and metasomatic phenomena in the polymetallic skarn deposits of western Karamazar” [V.A.Zharikov, 1959], the work of V.A.Zharikov and B.I.Omelianenko, “Some problems in the study of the changes in the embanking rocks in connection with metallogenic research” [1965], “Skarn deposits” by V.A.Zharikov [1968], “Geological and physico-chemical regularities of propylitisation” by V.L.Russinov [1972], “Petrology and geochemistry” by P.V. Koval’ [1975], “Metalliferous hydrothermal changes of rocks” by B.I.Omelianenko [1978]. Other articles study the difference between metasomatic formations, among them the theory of metasomatic zoning. For

instance D.V.Rundkvist and others “Greisens deposits” [1971], I.P.Scherban “Conditions of formation at low temperatures of metalliferous metasomatites” [1975],) G.T.Volostnih “Argillization and mineralization, U.V.Kazitsin “Metasomatoses in the crust”, “Baikal metalliferous metasomatites” [1972, 1979], V.G.Kushev “Precambrian alkaline metasomatites” [1972], and many more.

Anyhow, by the end of the seventies all the main types of metasomatoses were described, their mineralogical composition studied, as well as their parageneses, the structure of their deposit, and one or other degree their genetic peculiarities had been elucidated. In other words the “formal” description of metasomatoses had been nearly completed.

In the seventies, research on metasomatic processes was oriented in a new direction: experimental modeling of metasomatic zoning by V.A. Zharikov, G.P. Zarausky and I.P. Ivanova. All the main types of metasomatoses were reproduced in the past 20 and some years: alkaline metasomatites, lime and magnesian skarns, greisens, andalusite and sulphurous quartzites, propylites, breccias, argillites etc. For many metasomatic formations were determined the boundary conditions of their formation (in relation to P,T, activities of H_2O , CO_2 , S, HCl, KCl, NaCl and other components) were established the growth speeds of diffusion columns and the necessary conditions to the flow of the infiltration metasomatism. In particular, many important researches in experimenting metasomatoses were carried out at the Institute of Experimental Mineralogy (IME) in the laboratory of G.P. Zarausky, in whose book “Zoning and formation conditions of metasomatic rocks” (1989) is collected important original material and is provided sufficient bibliography. The works on experimental modelings of metasomatic displays have practically no counterparts in foreign researches.

Another new direction in the development of D.S.Korzhinsky’s theory of metasomatic zoning, is aiming at quantifying determination of the parameters of the equilibrium phases in the locally equilibrated metasomatic columns, reproduced on EVM. Possibilities of quantifying the dependence of metasomatic parageneses upon temperature, pressure and activity of the components in the solution have appeared, thanks to important results in theoretical and experimental researches. Firstly, there was provided a systematic experimental study of the main rock-forming systems under conditions of a perfectly mobile regime of H_2O , CO_2 , HCl and NaCl [Zharikov et al. , 1972; Ivanov, 1984; Hemley et al.1961; Frantz and Popp, 1979, 1980; Zharikov, 1991 and many others]. These researches have permitted not only to define the stability field of the main parageneses of metasomatic rocks, but also to obtain from experimental data, the thermodynamic characteristics of minerals and their components for high parameters. It was also important collectively to utilize the known thermodynamic characteristics of the simplest minerals [Robie and others, 1978; Naumov and others, 1971].

Other researches played perhaps a decisive role in the calculation of metasomatic reactions. They consisted in elaborating methods to calculate the thermodynamic characteristics of components of aqueous solutions of electrolytes for high parameters. Many researchers took part, but G. Helgeson's works played the leading role [Helgeson and Kirkham, 1974, 1982; Helgeson and others, 1978; etc.].

Finally a direct step towards calculation of metasomatic columns was made by U.V.Shvarov [1976], who elaborated a program of calculation of the composition in equilibrium in a multi-component hetero-phasic system (Gibbs program). Further application of the equilibrium model in the diverse zones of the metasomatic column (method of successive reactors) yields an image of the metasomatic zoning and its quantitative parameters. This Gibbs program calculation using approach of successive reactors has been successfully employed to analyze various metasomatites, notably in peri-ore [Ivanov et al., 1979; Ivanov and Borissov, 1980; Grichuk et al., 1982, 1984; Rizhenko et al., 1977 etc.].

In the history of the development of metasomatic zoning theories are outstanding several publications especially devoted to in-depth analysis of equations of metasomatic zoning, their mathematic content, in search of a possible quantitative solution, especially of the more complex cases of metasomatism [Balashov, 1985, 1992; Demin and others, 1979; Zarausky and others, 1989; Frantz and Mao, 1976; Lichtner, 1991; Lichtner and Balashov, 1993; Guy, 1993; etc]. A new direction of research develops also in the modeling of periodical zoning resulting from auto-organized metasomatic systems [Roussinov and Zhoukov, 1994].

When research appraising the domain of metasomatism, it is easy to see that at the time of the last generalizations [Korzhinsky, 1953; Zharikov and Omelianenko, 1965; Omelianenko, 1978], an enormous material has accumulated either in the study of separate metasomatic formations or in the theory of metasomatism. A new direction consisted in experimental and computerized modeling of metasomatic processes. It has therefore appeared essential and expedient to write a new collated book propounding the basis of the contemporary metasomatic theory, a brief general characteristic of the main types of metasomatism and showing the contemporary views about the ties between metasomatism and magmatism, mineralization and other geological phenomena.

The present book pursues these aims. Unlike earlier generalizations, the present monograph was written by many authors under the direction of V.A.Zharikov and V.L.Russinov. The first, theoretical part is due to V.A.Zharikov (chapters 1-3), N.N.Pertsev, for paragraph "Crystallization pressure" in chapter 2), chapter 4 by V.L.Russinov, chapter 5 by G.P.Zarausky. Part II, dealing with interactions between metasomatism, magmatism and

metallogenesis, was written by A.A.Marakoushev using data from U.B.Shapovalov (chapters 6, 9, 10) and V.L.Russinov (chapters 7, 8, 11). Part III propounds principles of classification of metasomatic rocks; their systematic is presented by B.I. Omelianenko in chapter 13 and in chapter 14. V.L.Russinov presents the physico-chemical systematic of metasomatic formations. Then chapter 15 by I.T.Rass gives the main features of metasomatic formations and types of metasomatic processes, the metasomatites of alkaline-ultrabasic magmatic complexes and the phenites. Chapter 16 by V.A.Zharikov, N.N. Pertsev, K.V.Podlesky gives the skarns, chapter 17 by V.L.Russinov, with paragraphs by G.P.Zaraisky, the greisens, chapter 18 by V.L.Russinov the propylites, chapter 19 by S.S. Abramov the secondary quartzites, chapter 20 by O.V. Andreeva the beresites, chapter 21 by B.I. Omelianenko the alkaline metasomatites, chapter 22 by V.L. Russinov with paragraphs by M.S.Seredkin, chapter 23 by O.V.Andreeva with one paragraph by V.A.Golovina the argillites, and chapter 24 by Russinov with paragraphs by B.I.Omelianenko the crumpled metasomatic zones and the abyssal fractures.

Recruiting so many collaborators had not only positive sides but also definite difficulties. The positive element was obvious: each section was written by a specialist who for many years had successfully worked with these problems. Each author's individuality in turn made impossible a complete uniformity in the designation of material when characterizing the various metasomatic formations. However, the chief complication consisted in the different treatment by the different authors of some complex genetic questions. This does not touch the foundation of the theory of metasomatic zoning. Here the authors were unanimous not only in admitting its essence (about which there can be no doubt), but also its important methodological significance for the comprehension of metasomatism. Disagreements occur about not particularly demonstrated adjacent questions: the links between magmatism, metasomatism and metallogenesis, or the origin of metalliferous solutions, the cause of mineral precipitation. This remotely recalls the famous discussion in the twenties on the role of an acid gas and an alkaline solution in metallogenesis (cf. T.S.Lavring "Nature of the metallogenic fluid"). This question particularly concerns the causes of evolution of the postmagmatic processes. It appeared more than once even, after the mentioned discussion and after the hypothesis was uttered by D.S.Korzhinsky (1957) of acid hydrothermal differentiations (see references in the corresponding chapters). This, probably, objectively reflects not only the complexity of the problem but also the multiplicity of possible mechanisms.

Elements of discussion of these and a few other genetic problems are not to be considered as insufficiencies of the book. The existence of different viewpoints (if sufficiently established) undoubtedly permit the essence of the phenomena to be comprehended.

We hope this book will rise interest and prove useful to large circles of specialists.

V.A Zharikov

V.L.Russinov

Part I

Theoretical bases of metasomatism

Chapter 1

General presentation of metasomatism

1.1. Definition of metasomatism

Metasomatosis, metasomatism and metasomatic processes are practically synonymous. Nevertheless some researchers mean by metasomatosis separate metasomatic processes (potassic metasomatosis, sodic metasomatosis, etc.) whereas by metasomatism they mean an aggregate of metasomatic changes as a whole. There exist several definitions of metasomatism, but the most complete appears to be the following, which in principle corresponds to the notion of metasomatosis formulated by D.S.Korzhinsky [1955].

Metasomatic processes: such processes develop in rocks and ores; they can occur through substitution of minerals to others, entailing changes in the chemical composition of rocks or ores; these changes are produced under conservation of the solid state of rocks or ores as a whole, under the action of fluids linked with inner endogenic processes in the earth.

This exhaustive definition singles out metasomatism amid other endogenic processes. Above all is indicated the means or mechanism of realization of the process: through replacement of a mineral by another.

This question will be addressed below in more detail, but it may already be noted that liquefaction of minerals and simultaneous precipitation at this place of another or several other newly formed minerals have a sharply predominant, commanding significance.

For example pseudomorphoses may be observed as necessary presence in metasomatites usually resulting from the formation of some minerals newly formed on the pre-existing mineral. This peculiarity of the metasomatic process is known as the “rule of constant volume in metasomatosis” long since formulated by V. Lindgren [Lindgren, 1925]. It seems that another mechanism, change of an ion into another, may be alleged in case of replacement of minerals

of proximate volume and structure. But J.Wyart's curious experiments [Wyart and Sabatier, 1956] with sodic solution enriched with $\delta^{18}\text{O}$, have shown the replacement of adulaire by albite to be due to a mechanism of liquefaction - precipitation.

A second, very important definition of metasomatism as a process arising with preservation of the solid state of the rock as a whole, is that the volume of pores occupied by the solution is negligible compared to the volume of the rocks, and that the whole matter in the pores is found in liquid condition. This property of the metasomatic processes radically distinguishes them from magmatic phenomena and from the filling up of voids or open fractures. Crystallisation of melts or from fluids in a free volume (slopes, open fractures, etc.) proceed along eutectic and eutonic principles contrary to the proper tendency of metasomatism. We shall demonstrate below but may already point out that the characteristic feature of metasomatism development is a tendency for the number of minerals to diminish and for monomineral rocks to appear in the course of the process. On the contrary the eutectic-eutonic principles augments the number of minerals in the course of crystallisation.

Metasomatism, as defined, entails variation in the chemical composition of the initial rocks and the formation of new rocks, while is changed the content of some petrogenetic (and ore) components. The formation of rocks in which only water and carbonic acid are exchanged, i.e. in which reactions of hydration-dehydration, carbonation-decarbonation occur, is not a form of metasomatism but are traditionally related to metamorphism. Intrusion or removal of H_2O and CO_2 belongs to metamorphism. Intrusion or removal not only of H_2O and CO_2 but also of other components belongs to metasomatism. Such is the generally accepted boundary between metamorphism and metasomatism.

Other opinions exist however about the delimitation between metamorphism and metasomatism: V.S. Sobolev [Facies of metamorphism, 1970] alleges the high extension of metamorphic processes, with alkaline content variations (usually in intrusion); considered possible to distinguish between metamorphism, alkaline metamorphism and metasomatism. According to other studies there correspondingly appear in the metamorphic processes other content variations not only of alkaline but also of other components [Krilova & *al.*, 1972; Davidchenko, 1983; Glebovitsky & Bushmin, 1983]. Therefore metamorphic and metasomatic processes must be strictly delimited, not according to variations of content but rather to the thermodynamic regime of the components. To metamorphism are related processes in which H_2O and CO_2 are perfectly mobile; to metasomatism, those in which not only that occurs, but in which the same is true for other petrogenetic components (the alkalines, CaO , MgO etc. are perfectly mobile up to a regime of perfect mobility of all components). Moreover, metamorphism is sometimes used in a broad sense designating all the endogenous processes of transforming material in solid state.

Metasomatic processes occur under the influence of fluids. All peculiarities in composition and structure of the metasomatites depend on the influence of fluids, of regimes insuring the differential mobility of components. Respective paragraphs will show the physico-chemical part played by each fluid. Their influence is immediately to be seen in geological observations. Metasomatic changes are unequally distributed, their precise confinement in zones of tectonic dislocation and fracturation, contacts, the enormous addition and removal of materials unambiguously illumine the bond between metasomatism and the influence of fluids. In evaluating the latter's role in the transport of matter in metamorphic processes, V.Faif [Faif & *al.*, 1962] considered the alternative: either the temperatures of the metasomatic processes may grow beyond 1200°C (the diffusion speed in solid state becomes then geologically significant), or the transfer of matter occurs through fluids, proving these to play an exclusive part.

The fluids apt to produce metasomatism generally appear as hydrothermal solutions (or more rarely hydrothermal fluids), independent from the fact that they are found in an essentially liquid or super-critical state. Moreover, it is important to note that if we set aside the formations due to volcanic or subvolcanic activity, no essential difference can be observed in metasomatites between low, middle and high temperatures regarding their structure or additions or removal of matters etc. (neglecting finally important information about kinetic factors of the metasomatites in low temperature and at high scales of high temperatures). This testifies that metasomatism shows similarities with the properties of the liquids or “liquid-form” solutions. These solutions differ from gases through their great density, by the great solubility of components and noticeable their dissociation. On figure 1.1 a T-P diagram indicates the critical point of water, of the NaCl solution, of the “critical isochores” and the plotting of T-P parameters of gases-liquids, including from many hydrothermal ore deposits, according to the data of Naumov & Touranov [1969]. Although definition of the T-P parameters of the “gases-liquids” inclusions has notorious errors one can already conclude that most points are disposed in domains possessing properties of liquids.

New works have emerged in the last few years showing the possible role of a gaseous phase in the transfer of matter.

1.2. Types of metasomatic processes, their links with magmatism and metamorphism

Metasomatism arises under the influence of fluids: therefore for the appearance of metasomatic processes, addition and removal of matter for the peculiar structure of metasomatic bodies the manner of matter transfer into the solutions is of decisive significance. Consequently D.S. Korzhinsky [1950] has recognized two kinds, of metasomatism, diffusion and infiltration. To diffusion

metasomatic processes, are related those in which transport of components occurs through diffusion in an aqueous liquid. In infiltration metasomatism, transport of matter occurs in the flow of liquid as a result of its infiltrating or percolating through the rocks. Of course in natural conditions these extreme cases of metasomatism occur rarely and we usually have to do with both combined. However, the predominance of one or the other way of matter transfer is precisely expressed in the scales and structure of the metasomatic bodies. Essentially, the diffusion metasomatites, limited in their dimensions (decimeter, meter, rarely more), which clearly coincide with the fissures and contact surfaces, show gradual variations in the composition of their forming minerals and rocks. On the contrary, infiltration metasomatism may occupy significant masses of rocks with sharp changes in the composition of the metasomatites. Similarity and differences in structure between diffusion and infiltration metasomatites are examined further on.

To metasomatism proper are related processes linked with internal endogenous forces of the earth. Such limitation is conditional but seems fully well-grounded and this is why: replacement processes with variations in chemical composition also appear habitually in zones of “hypergenesis”. Only, factors such as low speed of reaction, kinetic parameters, influence of superficial forces, replacement of living organic matter etc, which have no decisive significance in endogenous metasomatism, assume essential significance. Therefore, the corresponding processes are better called especially **hypergenous metasomatism**. Even more conditional is the limit between endogenous metasomatic processes since they occur in the crust and in the mantle. In this case it is better specially to deal with **mantle metasomatism** since their main peculiarity depends on the fact that under mantle conditions the influencing environment proves to be the force of concentration of liquid brine very similar to melts.

Metasomatic processes in the crust are undoubtedly linked with magmatic manifestations. For some metasomatites this link is geologically evident: they appear in zones of occurrence of magmatic melts, contact zones or in very intrusive massifs. The link of other metasomatites with magmatism is established through geochemical symptoms and especially through the evolution of hydrothermal solutions predetermined by their magmatogenous nature.

D.S. Korzhinsky [1955] as he underscored the link between metasomatism and magmatism distinguished two great groups of metasomatic processes: I. Those in magmatic stages, and II. Those in postmagmatic stage.

To the first group belong the metasomatites formed in the surrounding rocks in periods of emergence and introduction of magmatic melts under the influence of solutions distinguished from the liquid magmatic mass. On the contrary, in the second group the processes occur after solidification and crystallization of the intrusive massifs they have a spatial link with, also

transforming the intrusive rocks. These processes are influenced by residual solutions issued from deeper magmatic chambers.

The post-magmatic metasomatic processes are in turn divided into three subgroups: II_a, processes in early alkaline stage; II_b, processes in the acid lixiviation stage and linked deposits; II_c processes in final hydrothermal stages.

An optimal subdivision of the post-magmatic metasomatic stages is based on the surprising geochemical singularities of hydrothermal postmagmatic processes. There are expressed in regular variations in the acid regime of the magmatogenous fluids. The fluids' acidity grows in these processes, reaches a maximum and then decreases.

This particular evolution of the fluids, linked with their magmatic sources, was first clearly formulated by D.S.Korzhinsky [1955, 1957] as a hypothesis on the acido-alkaline hydrothermal differentiation.

A few points should be underscored. First, should be remarked the essential part played by the acid hydrothermal fluids and their reaction to rocks (transfers and precipitation of metalliferous components) has long since and constantly been described in geological literature. Possibly the most brilliant difference of views appeared in the discussion in "Economic geology" at the end of the thirties [Greyton, 1946]. Acid gas or and alkaline solution, the main mineralizing fluids were always diversely interpreted, on the one side by K. Fenner, N. Boous etc., on the other by L.G. Greyton, K.Ross, D.Cheller, summarized and diversely compromised by E.Ingerson and J.Mori et and others.

Secondly, extensive geological experiments have shown that there exists a definite group of correlation between the various metasomatites, between them and ores when these are related to one geological cycle. For instance metasomatites of the skarn type always appear earlier than the greisens, or mineralization in beresites and argillisites lags and appears a little later than strictly perimetalliferous metasomatism. Many other examples of such correlations might be adduced, which generally is explained through influence of various fluids linked with their pulsating intrusions of different age and separation from the hearth.

The prominent novelty of D.S.Korzhinsky's hypothesis of acido-alkaline hydrothermal differentiation is that he succeeded in finding one main cause determining all the main peculiarities of the postmagmatic processes. The main factors appear to have been the regular change in the acidity of the very hydrothermal fluids, from alkaline to acid and vice-versa. Namely, this internal evolution of the fluids themselves brings about correlation in time and space between different metasomatites and between metasomatites and ores, and unites the acid and alkaline regimes of the solutions.

Other factors, namely temperature, depth, composition of the surrounding rocks appear more particular, determining the concrete habit of metasomatites

and ores but are no important mechanism in the evolution of post-magmatic fluids.

The theory of acido-basic evolution of magmatic fluids based on D.S.Korzhinsky's hypothesis is now widely accepted and sufficiently established from the physico-chemical viewpoint.

About their dependence upon the geological setting one can distinguish between autometasomatism, contact metasomatism, periveinous and regional metasomatism. They frequently succeed one another in time and space.

Autometasomatism (or **simple metasomatism** according to D.S.Korzhinsky) composes the apical parts and, near it, the veins which form in the magmatic bodies. It usually appears as small changes in great masses of magmatic bodies. Typical autometasomatic processes are, for instance, albitisation of granitoid intrusions or serpentinitisation of ultrabasic massifs. As appears in the designation, these processes are linked with an early post-magmatic stage.

Contact metasomatites are more diverse and specific. To begin with, the different skarn formations developed in the early post-magmatic stage in contacts of intrusions with carbonated rocks, or with enclosing aluminosilicated and carbonated rocks, when they were setted in a zone of a hot intrusion area. Skarn formations appear in contacts and in space, and in the genetic sense of the term, as far as their development is linked with the emergence of fluids into the zone of contact of a chemically unbalanced carbonated and aluminosilicated surrounding and their mutual reactions. Skarns are contact infiltrations and in this case, when the mutual reaction of two surroundings in unbalance has the supreme significance, it is bimetasomatic.

To contacts are related mighty processes called "lixiviation around contact" (D.S.Korzhinsky), evolving in the acid stage and occupying parts of contact intrusion and surrounding rocks.

The most brilliant example is given by the greisens and secondary quartzites. The metasomatic contact processes develop in space through contact lixiviation (towards the contact) and, in time, replace early stages of autometasomatism.

To periveinous metasomatites is related the type of metasomatites, propagated on long distances, linked with the formation of veins (and stockwerks) of mineralization. Part of them is called metalliferous, although in the conditions (an aluminosilicated surrounding) prevalent at the time of formation they do not much outstrip the ore-deposit. Perimetalliferous metasomatites develop in a large gamut of temperatures (from high to low temperatures) but are always linked with the acid stage of the postmagmatic process. However, morphologically, expressed metasomatism, such as the periveinous one, may develop in an other stage of the hydrothermal process.

Regional or areal metasomatism appears in various geological environments. Regionally distributed is the alkaline (K,Na) metasomatism of magmatic and the early post-magmatic stage in deep horizons of the crust. It also appears at moderate and even at small depth, in external zones where take place perimetalliferous processes such as greisenization, quartzo-sericitic metasomatism, propylitization and a few others. One should underscore well-known correlations: zones of intense metasomatism as a rule are bordered by zones of small changes, having areal extension. Later on, they appear on their turn within a deeper metamorphic area. As already pointed out, the difficulties to distinguish external metasomatic zones from those of metamorphism have their repercussion in defining alkaline metamorphism; one can add the problems of distinguishing external zones of propylitization and greenstone zones of metamorphic modification of volcanic stratas. On the other hand, all this finally reflects the close genetic link between metamorphism and metasomatism as a result of the action of hydrothermal fluids of magmatic origin. “There exists an indissoluble link between magmatic metamorphic, metasomatic and hydrothermal metallogenetic processes” (D.S.Korzhinsky, 1955, p.363).

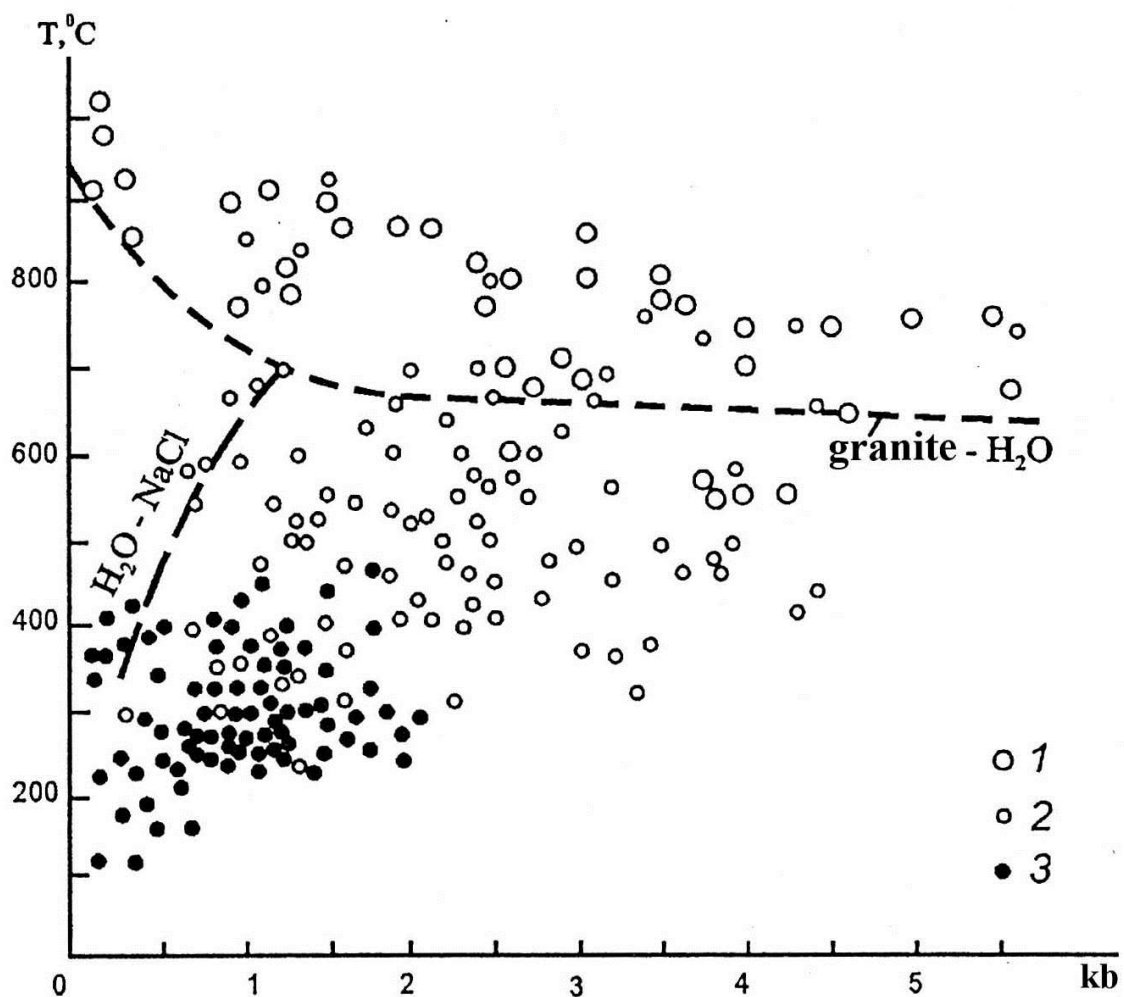


Fig.1.1. T - P curves of magmatic and metasomatic processes after data of research on liquid inclusions.

Dotted lines of solidus in the system granite-water and curve of bi-phased gas-liquid equilibrium in the $H_2O-NaCl$ system.

1- magmatic liquids; 2- postmagmatic fluids of granitoids and their metasomatites; 3- hydrothermal solutions of ore deposits after data of numerous authors.

Chapter 2

Thermodynamics of Metasomatic systems

2.1. Local equilibrium and types of metasomatic systems.

Equilibrium in metasomatic systems

The metasomatic variations of rocks and ores represent of course irreversible processes. Only, the peculiarity of the evolution of endogenic metasomatic processes consists in the fact that the variation of external parameters that bring about metasomatic changes occurs much more slowly than the processes of adaptation of the system to the varying parameters. It turns out, in this way, that at each instant, in each portion of extension of the system, equilibrium is completely reached with its determining parameters. This condition is called local equilibrium, an appellation proposed in the fifties by D.S. Korzhinsky [1950, 1957]. A little later appeared an analogue term, mosaic equilibrium, in monographs and textbooks of thermodynamics [Bazarov, 1961].

It must be especially noted that the notion of local equilibrium directly derives from the notion of thermodynamic equilibrium for the first time clearly formulated by D.S. Korzhinsky [1949, 1957]. It is traditionally understood, in thermodynamics, that a system is meant to be in equilibrium when its thermodynamic potential is minimal (U = internal energy, F = free energy, G = isobar potential, etc.), the state factors (the independent parameters) of the system being constant and the intensive parameters being equal in the phases. In such a system all the natural processes have taken place and the system stays invariable, inactive for constant state factors whose number equals $K+2$ in a simple thermodynamic system¹. Such a representation is unwittingly linked with the notion of equilibrium with perception of completeness of an exhausted, "atrophied" system. This was dealt with not only by the thermodynamicists, which gave rise to the notion of the "thermal death of the universe" [Krichevsky, 1962].

This is however absolutely not the case and D.S. Korzhinsky was the first in 1957, to underscore the fact that the notion of equilibrium unambiguously defines the interdependence of the system's parameters, but not at all their

¹ Among simple thermodynamic systems there are some in which only thermal, mechanical or chemical processes occur, and there is no electric, magnetic or others, which may besides also characterize similar thermodynamic correlations. In this simple system, the number of independent intensive parameters (f_{in}) and that of extensive parameters (f_{ex}) is equal to: $f_{in}+f_{ex}=K+2$.

behaviour. Somewhat changing Korzhinsky's formulation it can be said that, the system reaches its equilibrium when its thermodynamic potential is minimum, whose status is entirely defined by $K+2$ independent parameters (state factors or factors of equilibrium, another designation of independent parameters). With that, it is indifferent whether these factors are constant, or are in process of changing. It is important that, for each moment, the general state of the system be defined by $K+2$ unknown parameters, so that the system's thermodynamic potential be minimal. In other words, the relaxation speed of the system must be great compared to that of the state factors.

There exist rigorous proofs of complete equilibrium of the state of the system. This is the rigorous dependence upon the phase rule and of the law of distribution of the components between the phases in conformity to the equality of the chemical potential components in the phases. Nernst's equation of distribution is a partial variant of these correlations. Obviously, the state of total thermodynamic equilibrium possesses an absolute minimum of thermodynamic potential, i.e. there is no other phase composition for a given chemical composition of the system, which would have a smaller thermodynamic potential.

In natural conditions, the total equilibrium is of course a limit case in which are approached many particularly high temperature metasomatites. At the same time, thorough research always also exhibits cases of rupture of the total equilibrium, relicts of substituted minerals (breach of the law of phases), zonal crystals (rupture of equality of chemical potentials), etc and a few other signs. However, no evil without good, these deviations allow us to decipher the mechanism of metasomatic replacements.

The systems are defined in total equilibrium, as we have underscored, by means of $K+2$ independent parameters. For heterogeneous systems this is possible only when the dependent intensive parameters are equal in all the phases (the independent intensive parameters are equal for any system in conditions of its task, or, as it is said, of its existence facing the external medium). In the dependence of the metasomatic system upon the thermodynamic type, these necessary imposed conditions may be different: in a isotherm-isobar system such a condition is equality in the phases of the chemical potentials of the components; in the isotherm-isochore systems, besides equality of the chemical potentials, pressure must be the same for all phases.

Meanwhile, natural metasomatic processes, are noticeably characterized by conditions in which pressure of the fluid phase, fulfilling a porous volume and fractures in the rocks, is smaller than that exerted upon the solid rock framework. In this case the system is not yet in perfect equilibrium, since an independent parameter yet appears, the pressure of the fluid phase, and we find $K+3$ independent parameters in the system. Only, such a system may be for any long time stable if these $P^s \neq P^f$ correlations are maintained as conditions to the

existence of the system and if the system possesses, in this state, a minimal thermodynamic potential. We agree to naming this minimum, relative, reserving the term “absolute” for a system entirely in equilibrium with $K+2$ state factors. It is therefore more convenient to call “stable” any steady state with a number of $f_{in}+f_{ex} > K+2$ independent parameters (if they possess a relative minimum of thermodynamic potential) leaving the definition “equilibrium or total equilibrium” to a system with $K+2$ independent parameters and an absolute minimum of thermodynamic potential.

Stable systems (with $f_{in}+f_{ex} > K+2$), when in total equilibrium may find themselves in local equilibrium if relaxation of internal dependent parameters of the system can occur fairly more quickly than the variations of the $K+3$ (or any $f_{in}+f_{ex} > K+2$) external independent parameters. At every instant the system may have a relative minimum of thermodynamic potential (i.e. a minimal value of the state relatively to all the other phases for a given composition of the system and the given $K+3$ (or $f > K+2$) independent parameters). We remark, looking forward, that local equilibrium in a stable system with $K+3$ independent parameters is the thermodynamic model prevailing in natural metasomatic systems.²

Thermodynamic types of metasomatic systems

Natural systems are related to a particular type of thermodynamic systems with perfectly mobile components (SPMC systems). A thermodynamic model of natural systems was discovered by Korzhinsky [1963, 1940, 1950, and 1957]: it was a marked contribution to natural sciences. The existence in nature of a particular type of thermodynamic systems is reflected in a general geochemical law called « principle of differential mobility of components ». This law has a very general significance, governing matter transfer in whatever natural processes, forming minerals, rocks and ores processes metamorphism, metasomatism, magmatism and ore formation.

According to the principle of differential mobility of components, the components taking part in whatever geochemical process behave qualitatively in different manners: some behave inertly, with appearance of independent extensive parameters (the mass of the components, their composition or quantity in the system); others are perfectly mobile, with appearance of independent intensive parameters (chemical potentials of the components, their activities, concentrations, etc). This means that the equilibrium of minerals (and generally, of phases) in the system and the phase modifications depend not only on temperature and pressure, but also on the chemical potentials of the perfectly mobile components, whereas the number of phases is determined by that of the

² The term « non-thermodynamic » means « rapid »: relaxation must occur much more quickly. As the limit « much more rapid » would be equivalent to « instantaneous », but this does not exist in nature. « Rapid » means that in all methods available to us we do not observe divergence with the equilibrium criteria, or we may neglect a small divergence.

inert components (and other extensive parameters of the system such as in volume, entropy).

The principle of differential mobility of components, notably in metasomatic formations, is most striking and clear. The well-known regularity, if you will, the general law of metasomatism is the reduction of the number of minerals in the metasomatites in proportion to the growth of metasomatic transformations, depending on the changes of thermodynamic regime of the components, from inert state to perfect mobility. In chapter 3 we examine this general law, lying at the basis of metasomatic zoning.

In the definition of metasomatism appears the constancy of the volume of the system, more precisely its independence from the processes developing inside the system. Therefore the most general type of metasomatic systems is those with constant volume and temperature, with perfectly mobile components. In the diffusion processes, where the moving force of matter transfer is the difference in the chemical potentials of the components, the thermodynamic potential is in the form:

$$F_{m(dif)} = f(T, V, m_a \dots m_i, \mu_j \dots \mu_k)$$

$$F_m = -pV + \sum \mu_a m_a \dots \text{ (Integral form)} \quad (2.1)$$

$$dF_{m(dif)} = -SdT - pdV + \sum \mu_a dm_a \dots - \sum m_j d\mu_j - \delta Q_i = 0 \dots \text{ (differential form)} \quad (2.2)$$

where $m_a \dots m_j$ are the masses of inert components, $\mu_j \dots \mu_k$ the chemical potentials of the perfectly mobile components, δQ_i the uncompensated heat, a general expression of the system's irreversible processes. Equilibrium conditions in such systems is expressed by

$$F_m = \min, dF_m = 0 \text{ and } d^2F_m > 0 \dots \quad (2.3)$$

The complementary necessary condition, equality in the phases of dependent, intensive parameters:

$$p^A = p^B = \dots = p^F$$

$$\mu^{Aa} = \mu^{Ba} = \dots = \mu^{Fa}$$

$$\mu^{Ai} = \mu^{Bi} = \dots = \mu^{Fi} \quad (2.4)$$

The law of phases in an isotherm-isochore system (SPMC):

$$n_{T,V,M} = f_{in} + f_{ex} - r = k_i + 1 - r \quad (2.5)$$

For metasomatic infiltration processes the matter transfer is brought about by the flow of solution and fluid and that is why the independent parameters of the perfectly mobile components appear through their concentration or activity in the solution:

$$F_{m(inf)} = f(T, V, m_a \dots m_i, C_j \dots C_k)$$

$$F_m = -pV + \sum \mu_a m_a \text{ (integral form)}$$

$$dF_{m(inf)} = -SdT - pdV + \sum \mu_a dm_a - \sum m_j dC_j - \delta Q_i = 0 \quad (2.6)$$

(differential form)

or for a non-ideal solution:

$$dF_{m(inf)} = - SdT - pdV + \sum \mu_a dm_a - \sum \mu_j da_j - \delta Q_i = 0 \quad (2.7)$$

where $a \dots i$ are the inert components, $j \dots k$ the perfectly mobile ones. The conditions of equilibrium, the same (2.3), a_j is the activity of component j . But we note that the components' concentration do not appear in canonical thermodynamic parameters: dm constrained with dC multiplied by RT/C .

The main difference between diffusion and infiltration metasomatism consists in the fact that in diffusion the matter transfer can only occur towards the smallest chemical potential of the components, whereas in infiltration metasomatism the matter transfer in the direction of the flow of matter is unlimited (including introduction of matter in saturated solutions).

In metasomatic processes flowing with conservation of volume (more precisely with independent volume) a situation is usually found when pressure on the solid rock-frame is greater than the pressure of the liquid or fluid phase. In such a case one finds, as told above, also $K+3$ independent parameters in the system:

$$F_{m(dif)} = f(T, V, p_F, m_a \dots m_i, \mu_j \dots \mu_k)$$

and

$$F_{m(inf)} = f(T, V, p_F, m_a \dots m_i, C_j \dots C_k)$$

thus, accordingly:

$$dF_{m(dif)} = - SdT - p^S dV^S + V^F dp^F + \sum \mu_a dm_a - \sum \mu_j d\mu_j - \delta Q_i = 0 \quad (2.8.)$$

and

$$dF_{m(inf)} = - SdT - p^S dV^S + V^F dp^F + \sum \mu_a dm_a - \sum \mu_j dC_j - \delta Q_i = 0, \quad (2.9.)$$

where S means solid phases, F means fluid solution.

Systems with unequal pressure in the solid phase and in solutions are very wide-spread in nature; in particular, equilibrium processes and dynamic processes in these systems are essential for comprehending metasomatic and metallogenic processes.

Apart from the isotherm-isochore systems with SPMC, some metasomatic processes occur in isotherm-isobar conditions. They develop in the external zones of metasomatic aureoles, contiguous and transient to metamorphic aureoles. They distinguish themselves by an insignificant introduction and removal of matter, easily compensated by small changes of volume of the altering rocks. Correspondingly, for the state factors and the thermodynamic potentials:

$$G_{m(dif)} = f(T, p, m_a \dots m_i, \mu_j \dots \mu_k)$$

$$G_{m(inf)} = f(T, p, m_a \dots m_i, C_j \dots C_k)$$

$$G_m = \sum \mu_a m_a \quad (2.10)$$

$$dG_{m(dif)} = - SdT + Vdp + \sum \mu_a dm_a - \sum \mu_j dm_j - \delta Q_i = 0 \quad (2.11.)$$

$$dG_{m(inf)} = - SdT + Vdp + \sum \mu_a dm_a - \sum \mu_j dC_j - \delta Q_i = 0 \quad (2.12.)$$

The condition of the equilibrium $G_m = \min$, $dG = 0$ and $d^2G_m > 0$ for a heterogeneous system is carried out through equalizing the chemical potentials of the inert components in the phases.

$$\text{Law of phases: } n_{T,p,m} = f_{in} + f_{ex} - r = k_i - r \quad (2.13)$$

Isotherm-isobar conditions can be established when pressure on the solid phase differs from that on the fluid one. For example, if the rocks are under lithostatic pressure and the fluid phase under hydrostatic pressure, i.e. $p^F \leq 0.37 p^S$, one member $+ V^F dp^F$ appears again in the equations 2.11 and 2.12 and the system will be stable for $K+3$ given independent parameters. However, there is a more suitable and general expression of the perfectly mobile state of a solution through the chemical potentials ($- m_{H_2O} dm_{H_2O}$) or the activities ($\mu_{H_2O} RT \ln a_{H_2O}$) of the aqueous phase in its components.

2.2. Fluid – rock equilibrium in metasomatism

Pressure of solution and mineral phases in the system

In natural conditions different relations appear between pressure on the liquid phase (solution, fluid) and that on the solid phases, minerals (mineral's crystallization pressure). The latter usually means pressure exerted by the mineral in its crystallization from the solution upon the environment (or, on the contrary, by the solid milieu on mineral's braising).

In the upper layers of the crust, are usually admitted lithostatic pressure of the mining rocks and hydrostatic pressure of the aqueous solution. Let us take the average density of the sedimentary and the weakly metamorphic rocks to be about 2600 mg/cm^3 ; that of water 1000 mg/cm^3 : then the relation between the two is $p^F = 0.385 p^S$. Hydrostatic pressure determined by that relation; presupposes the existence of a continuous vertical column of solutions, but this is rarely the case near the surface.

The relation $p^S > p^F$ is the most general for large variation within the limits $p^S \geq p^F \geq 0.385 p^S$ depending on the depth, the source of the fluids, the rock's permeability and other physical parameters. The usual natural relations are presented in fig. 2.1, a diagram showing depth (p^S), pressure of the porous solution (p^F) after measurement of the pressure of the plastic water and the T-P homogenization of the inclusions. Depth is estimated on geological data.

A limit case is when the pressure on the fluid phase is equal to that on the solid phase, $p^F = p^S$. This condition is brought about by crystallization in the presence of a free volume of water (in cavities and fissures) in superficial reservoirs, or, on the contrary, for high T and P in an excess of solution when its pressure ensures the equality of pressures on all the phases (for example, in an instrument for high parameters under pressure of water vapor).

Situations known and discussed under the name of autoclave effect it occurs when pressure of the fluid is higher than that of the surroundings. However, one must consider, firstly, that for the system as a whole, this metastable state is held up by a robust impenetrable envelope. Volcanic explosions and ejections, geysers, etc. point out the system's tendency towards a

stable state. Secondly, it is important to understand that, in violation of the metastable state, pressure on the solid phase within the autoclave equals that on the fluid phase.

The relation between pressure on the mineral and on the fluid phase is directly linked with the components' concentration in the solution. Let's take for simplicity's sake a mineral K with one component, braised in a volume V . From equation (2.8) we may conclude by means of cross differenciation:

$$(\partial p / \partial \mu_k)_V = (\partial m_k / \partial V) \mu_k$$

and, with passing to the complete derivative and the final increase (all other parameters remaining constant), we get

$$dp = \Delta m_k / \Delta V \times d\mu_k = d_k RT \ln a_k \quad (2.14.)$$

and for an ideal solution

$$dp = d_k RT \ln C_k \quad (2.15.)$$

and integrating between the limits p^k and p^F and, correspondingly, $C_k C_k^\circ$, we get

$$p^k - p^F = d_k RT \ln C_k / C_k^\circ \quad (2.16.)$$

where p^F is the pressure of the fluid phase in the free volume (more exactly for $p^F = p^S$); C_k° is the concentration saturation of the solution in component K for a pressure of the solution ($p^F = p^S$); p_k is the pressure on the solid phase, C_k is the concentration of the component K corresponding to the equilibrium with the mineral K at pressure p_k , d_k is the molar density of the mineral.

From the obtained relations an important conclusion is that at high pressure on the solid phase, when p^F remains independent, i.e. $p^k > p^F$, the concentration of component K in the solution surpasses that of saturation (C_k° , when $p^k = p^F$). In other words, with correlations ($p^k > p^F$) usual for metasomatism, the solution is supersaturated. This means that "metasomatizing" solutions infiltrate the voids, the fissures (or rapidly soluble minerals), and they immediately fill (or replace) them up to stability conditions $p^k > p^F$.

For the minerals with several components, summing up the right parts of the equations, one gets:

$$dp = \sum \Delta m_k / \Delta V \cdot d\mu_k = d_k \cdot RT \cdot d \ln a_a \dots a_k \cong d_k \cdot RT \cdot d \ln C_a \dots C_k = d_k \cdot RT \cdot d \ln \Pi \quad (2.17)$$

where Π is the solubility product. Integrating, we get:

$$p^k - p^F = d_k \cdot RT \cdot \ln \Pi / \Pi^\circ \quad (2.18.)$$

From which it follows that we get these correlations: crystallization pressure of a mineral depends on the degree of supersaturation of the solution by the corresponding components and vice-versa. In general metasomatism ($p^k > p^F$) the solutions are in equilibrium with the environing rocks and are supersaturated if they are saturated, as we have determined, in the conditions $p^S = p^F$. The influence by metasomatism of supersaturated solutions is amongst the most important metasomatism processes; Lindgren's rule of constant volume is by them defined in detail.

Here is an instructive example of mineral formation when pressure on the solid phase differs from that exerted on the fluid phase. Let some cavity of volume V be partly filled with a fluid (p^F) issued from the surrounding rocks which are under a pressure ($p^S > p^F$) greater than in the cavity; enters a solution with perfectly mobile components, j , h and k , for which we take the correlations $C_k/C_k^\circ > C_h/C_h^\circ > C_j/C_j^\circ$. For simplicity's sake, let the perfectly mobile components form their own minerals with one component, J , H , K . In a state of equilibrium, $F = -pV = \min$ and $r = f_{ex} = 1$, and the cavity must be filled with a single mineral possessing the greatest crystallization pressure and built components in a highly supersaturated solution (equation 2.16). However, the process takes place in stages. We show it in more detail utilizing the diagram fig.2.2: pressure (of crystallization and of the solution); volume (in its section, naturally). On entering the free cavity, the solution is supersaturated regarding all the components (j , h , k) and from the solution all the supersaturated minerals will crystallize quantitatively (at the limit O/I) in proportion to their degree of supersaturation $K > H > J$. Proportionately, part of the cavity, as shown on fig. 2.2) or all the cavity will be filled with the minerals, pressure will exceed $p^I = d_j RT \ln C_j$ as far as crystallization pressures p^k and p^h exert a higher influence on the mineral J . The latter will be replaced by minerals H and K quantitatively in proportion of the solution's supersaturation. There results formation of zone II built by of the minerals K and H at pressure p^{II} , somewhat greater than pressure p^H as far as p^K possesses a greater crystallization pressure than p^H , but in that zone lesser than full p^K (zone III) owing to precipitation of component H replacing component J . Finally, total replacement of mineral H occurs at the limit II/III and the rear zone in equilibrium will be built only by mineral K , developing a greater crystallization pressure $p^K - p^F = d_k \cdot R \cdot T \cdot \ln C_k/C_k^\circ$. An elevation of p^H up to p^{II} in zone II is linked also to the removal of component h from zone III. Such peculiar filling of voids, of fissures through metasomatism occurs mostly for $p^S > p^F$.

Some important consequences:

Firstly, supersaturated solutions entirely preserve in metasomatism the solid state of the rock as a whole (law of volume constancy): the cavities created through dissolution, the fissures refill immediately with minerals and the solution dries up.

Secondly, the cavities and fissures filled with the solution's minerals are submitted to "autometasomatism" in the sense that the precipitated minerals are in turn replaced by another precipitated mineral developing a greater crystallisation pressure, right up to monomineral formations of the most supersaturated components of the solution.

Thirdly, the growth of big crystals favours reduction of the system's free energy. From $F = -pV$, where $p = A / q$ pressure, the force A exerted by the

solution on the mineral's surface (q), one immediately sees that bigger crystals are thermodynamically preferred, the other conditions being equal³.

A more detailed discussion will require complementary data on surface energy of crystals, its dependence on the grain dimension, an examination of the link between the size of the crystals and the supersaturation concentration and other kinetic parameters. Let us note here a notable natural peculiarity, the growth of big crystals in the dissolution processes of mineral aggregates, astounding druses of gems grow in the process of formation, when the solutions are non-saturated enough relatively to the small crystals and slightly supersaturated relatively to the big ones, of which the grains keep growing.

Crystallization pressure and surface tension in metasomatism.

Pressure capable of developing crystals on their own is an essential factor in metasomatism. D.S.Korzhinsky surmised that its cause was to be sought in the monomineral "tendency" of metasomatic rocks. Pressure, as intensive parameter, must develop in equilibrium in the whole system. Therefore in isobaric systems crystallisation pressure must in principle be equal to the total pressure for all minerals. Metasomatic processes often develop in constant volume. If in such an isochore system is brought about a reaction in which the volume of the newly formed minerals is less than the volume of the initial mineral association, three different cases result.

1. Metasomatic contraction, or retreat under the influence of outer pressure exerted by the enclosing rocks [Korzhinsky, 1993] as for example in the formation of plagioclases with corundum.

2. Growth of porosity, appearance of pockets.

3. The most usual case is the appearance of a supplementary mineral refilling the liberated volume; for instance, calcite crystallisation replacing phlogopite in the metasomatic bodies formed in phlogopite deposits. In all those cases reduction of crystallisation pressure in the processes of mineral formation is compensated either (1) by fracturation of surrounding rocks with transition to an isobar process, or (2) by formation of voids, or (3) by deposition of a supplementary mineral simultaneously with the liberated volume, and transition, as in (1) to an isobar system.

If the volume of the products of the reaction exceeds the initial volume, there develops a crystallisation pressure exceeding the external one. This is linked with a rigid limitation of the system's volume. The significance of volume conservation, i.e. the isochore character of the system with development of crystallisation pressure is tested for the water-ice system. In isobaric

³ N.B. There is here confusion between free energy F and force F !

conditions, water in open tanks coagulates under pressure of about 1 atm., equal to crystallisation pressure. In isochore conditions, for instance in a filled pit under a road carpet, at congealing ice a sufficient pressure develops to destroy the carpet and swell the asphalt. In a solid recipient with water at -20°C ice forms the colossal pressure of about 5 Kbar (a big earthquake occurs under accumulated effort of only about 0.5 Kbar, i.e. in a lesser order of magnitude). Either the recipient does not resist such pressure and breaks, or keeps its initial volume with more compressed water and ice.

The full internal energy (U) develops in this simple system as total thermic energy TS, mechanical energy (work) in the system (PV) and chemical energy:

$U = TS - PV + \sum \mu m$, where T is absolute temperature, S the system's entropy, P pressure, V volume of the system, μ the chemical potentials of the components, m the molar quantities of the corresponding independent components of the system.

Gibbs's free energy (G) or isotherm-isobar potential constitutes only the system's "chemical" energy $G = U - TS + PV = \sum \mu m$, the most important datum for our value, as notably G is tabulated in the reference works of Robie & al. (1978). The isotherm-isochore potential or Helmholtz's free energy is given by

$$F = U - TS; \text{ or } F - G = -PV; \text{ hence } F = -PV + \sum \mu m$$

Further passing to the open system, i.e. to the system with inert and perfectly mobile components we get precise expressions of Korzhinsky's isotherm-isochore potential F^0 :

$$F^0 = F + \mu_a m_a + \dots + \mu_c m_c,$$

where a,...,c are the inert components i [Korzhinsky, 1977]. Thus, introducing F into $G = \sum \mu m$, we get

$$F^0 = -PV_{TB} + \mu_f m_f + \dots + \mu_k m_k,$$

where f,...,k are the inert components. The physical sense of this expansion in nature of the system consists in a limited volume of solid phases through free infiltration of solutions through the limits of the volume, for chemical potentials of perfectly mobile components outwardly fixed and equal in all parts of the system (the chemical reaction advances more slowly than the transfer of perfectly mobile components).

In conditions of equilibrium, the change of free energy $dF^0 = 0$; this opens the way to calculation of pressure at a given temperature in an isochoric system. Let us consider the concrete example of titanite formation in place of an association of quartz and rutile, calcicium being perfectly mobile in the solution infiltrated at 800K (526.8°C).



$$G^{800}_{\text{reaction}} = G^{800}_{\text{tit}} - G^{800}_{\text{qtz}} - G^{800}_{\text{rut}} = -109.983 \text{ kJ/mol}$$

[Robie et al., 1978]

$\mu_{\text{CaO}} = G_{\text{CaO}} + RT \ln a_{\text{CaO}} = 0.0083143 \text{ kJ/mol}$; $\ln(a_{\text{CaO}})$ is the natural logarithm of chemical activity of CaO. If for convenience we express natural logarithm in decimal, then

$$\mu_{\text{CaO}} n_{\text{CaO}} = 0 + 0.0083143 \times 800 \lg a_{\text{CaO}} = \lg a_{\text{CaO}} \text{ kJ/mol} \times 0.4343$$

$$V_{\text{TB}} = V_{\text{tit}} - V_{\text{qtz}} - V_{\text{rut}} = 5.565 - 2.2688 - 1.882 = 1.4142 \text{ kJ/mol}$$

Thus, $p = G_{\text{CaO}} - 1\mu_{\text{CaO}} = (-109.983 - 15.315a_{\text{CaO}}) \text{ kJ/mol} = 107.207 - 1.4142 \text{ kJ/mol}$

For a 1 bar pressure the activity in equilibrium of the CaO is $10^{-7.18}$. For a slightly higher activity, say 10^{-7} , crystallization pressure of titanite in an isochore system is gigantic, 1.963 kbar. A model for such a system can be represented, for instance, by a quartzite mass traversed by a porous fluid, where the CaO activity is 10^{-7} , not sufficient for the formation of a calcicium-constraining silicate (for instance, wollastonite for $T = 800\text{K}$ and 1 bar $a_{\text{CaO}} = 10^{-6}$), but higher than necessary for the formation of anorthite in association with quartz + sillimanite ($a_{\text{CaO}} = 10^{-8.61}$). Let there be in the quartzite a parcel of rutile inclusions. The fluid, as it crosses this parcel (geochemical barrier) will crystallize titanite with an enormous pressure of crystallization. This pressure sharply increases the quartz's and the rutile's solubility, which will liberate volume for titanite until total disappearance of one of them. Another scenario is possible: the enclosing rock doesn't resist an enormous pressure, it gets fractured or moves, which can increase the system's volume, in which runs a reaction and pressure decreases. Also possible is a combined development of both, fracturation and dissolution.

In isochoric metasomatic systems there easily occurs a dissolution of minerals, steady but with less crystallization pressure, liberating volume for the minerals with less crystallization pressure. This mechanism operates at the formation of metasomatic zoning accompanied with a monomineral tendency in the rear zone. In the closed systems where no chemical exchange occurs with the milieu, the condition of constant volume doesn't end up in a quantitative decrease of the coexisting phases; for instance the metamorphogenic alpine veins, filled with closed fissures, are born in the absence of an intense movement of fluids and matter transfer.

In terms of crystallisation pressure, one can examine the formation of many symplectites, grids and other regular or irregular crystal germinations. Within the limited volume, rocks may begin crystallising a new mineral according to external conditions of mineral variation. But the volume is already full of pre-existing minerals. If this new mineral's pressure exceeds that of one of the preceding minerals, the latter will begin to be replaced by the newcomer, no matter whether these minerals share components. This is frequently observed: needle germination (for instance, sagenite rutile in quartz, ludvigite needles in calcite, amphibole needles in quartz, fibrolite filaments in quartz, etc). The appearance of a germ of new mineral in the pores brings about a local strain

in the mineral-host, a local distribution of it, and a free volume for the new mineral. Various crystal grains, in various conditions, have in principle a somewhat distinctive pressure. The difference must however be sufficient to "pierce" the grain of the crystal-host, with the appearance of a greater crystallisation pressure in these cases of rapid growth. If a newly formed mineral contains inert components lacking in the mineral-host and liberated by the reaction due to the changing condition, such a replacement may be limited, with conservation of the mineral-host (as in sagenite) in connection with the content of inert components in the rock. With a common inert component, replacement may be only partial if inert components in the mineral-host do not suffice for a complete replacement.

In connection with crystallisation pressure there are the problems of the influence of superficial tension. The latter, in solid substances, summons forces of attraction of atoms in the crystalline net, which hinders the detaching of atoms and their gathering at the crystal's surface. In principle, superficial tension η in the crystal in various grains may be a little different and depend also on temperature. It is measured in J/cm^2 . For weak, easily soluble bindings, for instance NaCl (grain $\{100\}$) at 200°C , one has $\eta = 1.5 \times 10^{-5} \text{ J}/\text{cm}^2$; for strong bindings, such as diamond (grain $\{111\}$), one has $\eta = 114 \times 10^{-5} \text{ J}/\text{cm}^2$. Most minerals evidently occur in this interval. Surface tension has a physical sense of energy dissipated in forming surface mineral. So, in order to break a halite crystal one cm broad into cubes 0.1cm broad (surface 600 cm^2) an energy of $(1.5 \times 10^{-5} \times 594) \text{ J}/\text{cm}^2$ is needed. But, if from those small crystals is formed a primitive crystal, global energy decreases in that amount, i.e. a spontaneous process of increase of crystals takes place with energy release. Superficial tension may be expressed through abundant pressure (ΔP) on a solid phase. For instance, diamond grains of 1mm undergo an extra pressure of $114 \times 10^{-5} \times 0.001 = 114 \text{ bar}$ compared to a crystal of centimetric dimension. If the crystallization pressure for centimetric crystals equals the system's external pressure, the small crystals undergo pressure ($P + \Delta P$) so much higher as the mineral's grains are smaller. For micrometric grains ΔP may be high enough, from one to 100 bars, not to exert any substantial influence on the equilibrium. If big crystals in a system in equilibrium are in equilibrium with the solution, small crystals are out of balance with the extra pressure brought about by the surface tension. In a closed system may therefore appear spontaneous "recrystallisation", growth of big crystals and dissolution of small ones. In an isochoric open system may appear such a situation that big crystals have a greater crystallisation pressure than necessary for equilibrium, whereas small crystals have a negative one, i.e. they must dissolve. Moreover, removal of the dissolved matter may predominate over precipitation of big crystals, i.e. growth in big crystals occurs on a background of general matter removal. It is through such a mechanism that D.S.Korzhinsky has explained the growth in pegmatites of big crystals on the

walls of the dissolution cavity. That is apparently how arise veins full of calcite and nests with gigantic crystals of phlogopite and diopside in rocks with diopside and phlogopite [Pertsev & Koulakousky, 1988]. The increase of crystals along the path of fluids, as well as metamorphic recrystallisation (differentiation) induce for the most part a difference of pressure on small and big grains.

Particulars of solutions in microporous and microfissured surroundings

Metasomatic processes, we repeat, are provoked by solutions that appear in thin pores and fissures. General effective porosity and microjointing of compact eruptive and metamorphic rocks ranges from 0.2 to 1.2, rarely 1.5%. It is essential to evaluate the maximal and minimal dimensions of porous channels “working” in metasomatic processes. Numerous measurements of permeability of compact mining rocks [Shmonov et al., 1995; Shomonov & Vitovtova, 1992; Experiments in resolution of current problems of geology, 1986; Zharikov et al, 1990, 1993 et al.] imply dimensions of effective porous channels of 100 to 1000 Å (0.1 - 1.0 μm) and microfissures of 10 to 100000 Å (10 – 100 mμ). D.Norton and R. Knapp [Norton & Knapp, 1997] give similar dimensions, of so-called first pores, second microfissures. Experiments to defining permeability at increasing temperatures [Zaraisky & Balashov, 1995] show that on account of the anisotropy of the rocks’ thermic plasticity their permeability increases on an average in order (fig.2.3).

Another way of estimating the effective dimensions of porous channels may be based on the dynamic equilibrium of the minerals’ precipitation from supersaturated solutions owing to $p^S > p^F$ and, the contrary direction of the process of dissolution resulting from the high concentration of the solutions in equilibrium with the surface dispersed in minute pieces. These relations are defined by the equalities:

$$q \cdot dG + m_k \cdot d\mu_k \quad (2.19.)$$

and

$$- dG = m_k/q \cdot d\mu_k = \Gamma \cdot d\mu_k \quad (2.20.)$$

where G is Gibbs’s adsorption coefficient, showing superabundance of moles in the volume of the top layer. In a solution with many components the value Γ is, naturally, relative.

The behavior of solutions in ultraporous surroundings, with pores ranging in the order of μm demands a particular attention. As already remarked [Zharikov, 1976, 1995] in those conditions the solutions and their components behave otherwise than a free solution volume. Despite extreme actuality of this problem about direct or indirect reasons for formation of minerals and ore-deposits, experimental research was formerly isolated [Shmonov & al, 1984; Bielonozhko & Shmulovitch, 1986, 1987; Balashov, 1992]. Fig. 2.4 shows on

experimental and calculated data the distribution in molar values of carbonic acid between ultraporous spaces and free volumes of the solution ($\chi_{\text{CO}_2}^{\text{V}}$). From the equality of the components' chemical potentials we get:

$$\mu_{\text{CO}_2}^{\text{P}} = \mu_{\text{CO}_2}^{\text{V}} \quad (2.21)$$

$$\chi_{\text{CO}_2}^{\text{P}} \cdot \gamma_{\text{CO}_2}^{\text{P}} = \chi_{\text{CO}_2}^{\text{V}} \cdot \gamma_{\text{CO}_2}^{\text{V}} \quad (2.22)$$

and in the same way for water:

$$\mu_{\text{H}_2\text{O}}^{\text{P}} = \mu_{\text{H}_2\text{O}}^{\text{V}} \quad (2.23)$$

$$\chi_{\text{H}_2\text{O}}^{\text{P}} \cdot \gamma_{\text{H}_2\text{O}}^{\text{P}} = \chi_{\text{H}_2\text{O}}^{\text{V}} \cdot \gamma_{\text{H}_2\text{O}}^{\text{V}} \quad (2.24)$$

It is easily seen that for high pressures $\chi_{\text{CO}_2}^{\text{V}} > \chi_{\text{CO}_2}^{\text{P}}$ and accordingly $\chi_{\text{H}_2\text{O}}^{\text{V}} < \chi_{\text{H}_2\text{O}}^{\text{P}}$ ranging from 1.5 to 4 times (depending on T,P and pore dimensions). Owing to the significant dependence of $\gamma_{\text{CO}_2}^{\text{P}}$ and $\gamma_{\text{H}_2\text{O}}^{\text{P}}$ for porous solutions, the activities of the components, above all H₂O and CO₂, distributed between the minerals in equilibrium, may be very different from the real concentrations of these components in the finely porous surroundings. In the example dealt with (which has a fundamental significance with high parameters) when $\gamma_{\text{CO}_2}^{\text{P}} > 1 > \gamma_{\text{H}_2\text{O}}^{\text{P}}$ the water's molar fraction in the finely porous solution will be much higher and that of carbonic acid much lower than the values we have established for the mineral equilibrium. Disdain "particular" thermodynamic properties of solutions in finely porous surroundings has led, in particular, to a wide diffusion of errors on "dry metamorphism" and "dry fusion" for high parameters.

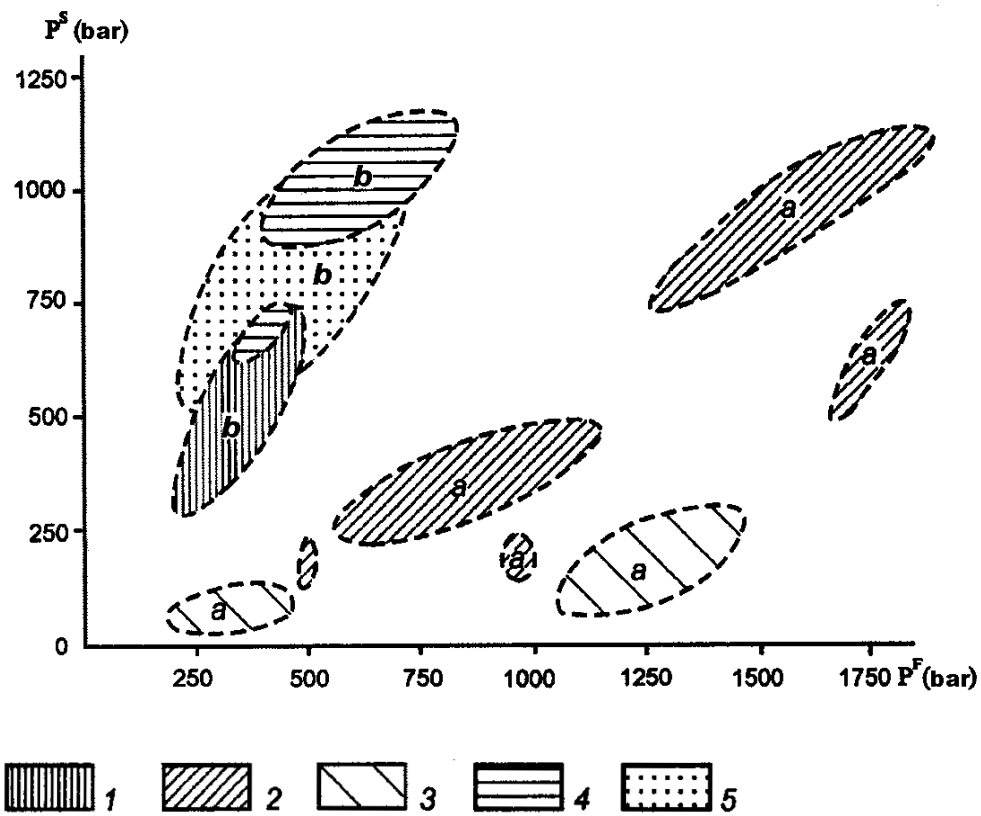


Fig.2.1. Correlation of lithostatic pressure and fluid pressure after data of inclusions (a) and measures of strata waters (b).

After data 1 of [Litvin and Tereshchenko, 1976]; 2 [Naumov and Tugarinov, 1962]; 3 [Prokofiev and Zorina, 1994]; 4 [Nechaev et al., 1987]; 5 [Fertl, 1980].

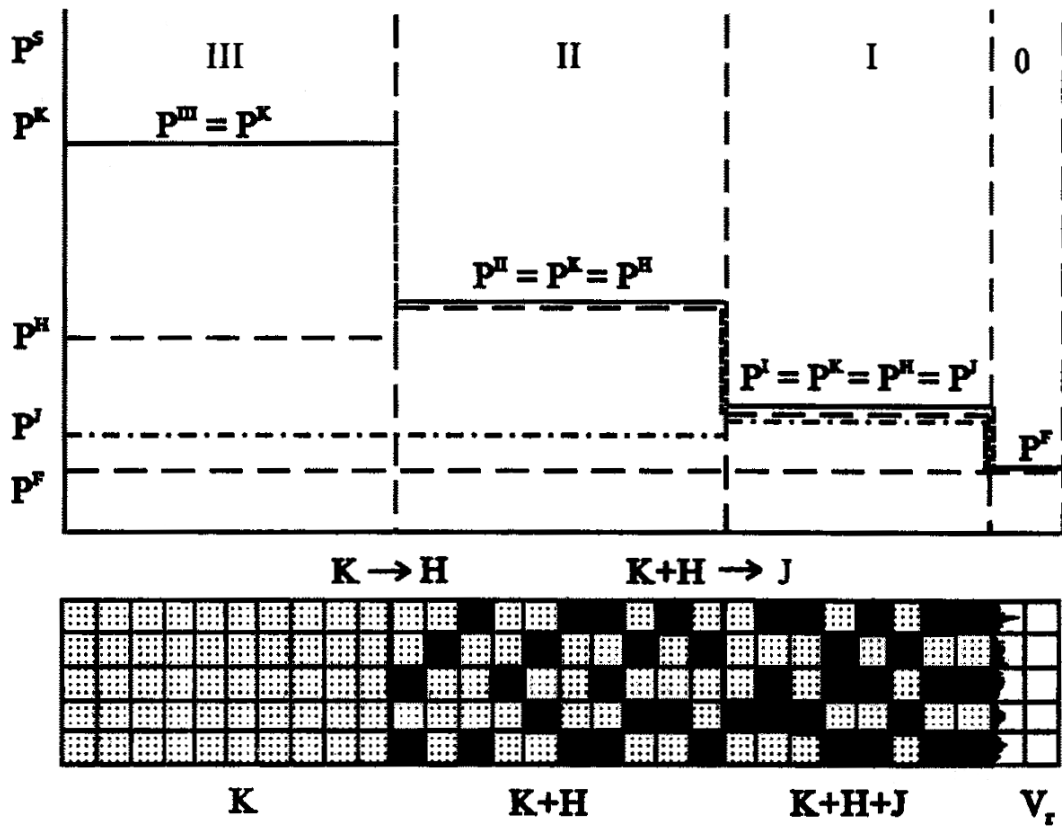


Fig. 2.2. Mechanism of cavity filling and autometasomatism.

V_r , remaining free volume of the cavity, P^F pressure of solution in free volume, P^K , P^H , P^J crystallization pressure of minerals in oversaturated solution.

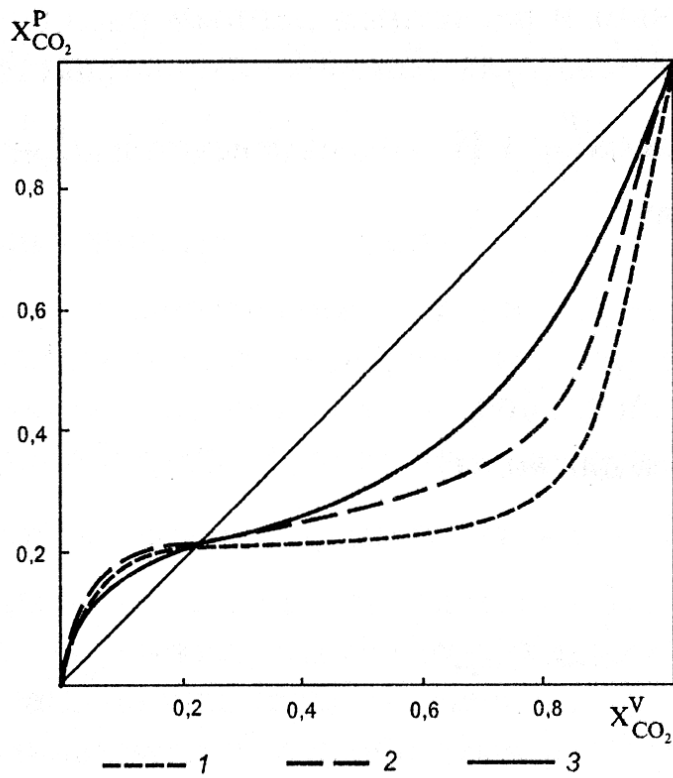


Fig. 2.3. CO₂ concentration in pores $X_{CO_2}^P$ and in free volume $X_{CO_2}^V$ of solution H₂O + CO₂.

1. 1000 bar, 400 °C , pores measuring $0.25 \cdot 10^2 \mu m$ in zeolites (experiment); 2 idem at 3000 bar, 600 °C (experiment); 3 calculated data for pores $0.08 \cdot 10^2 \mu m$ in quartz at 1000 bar and 800 °C.

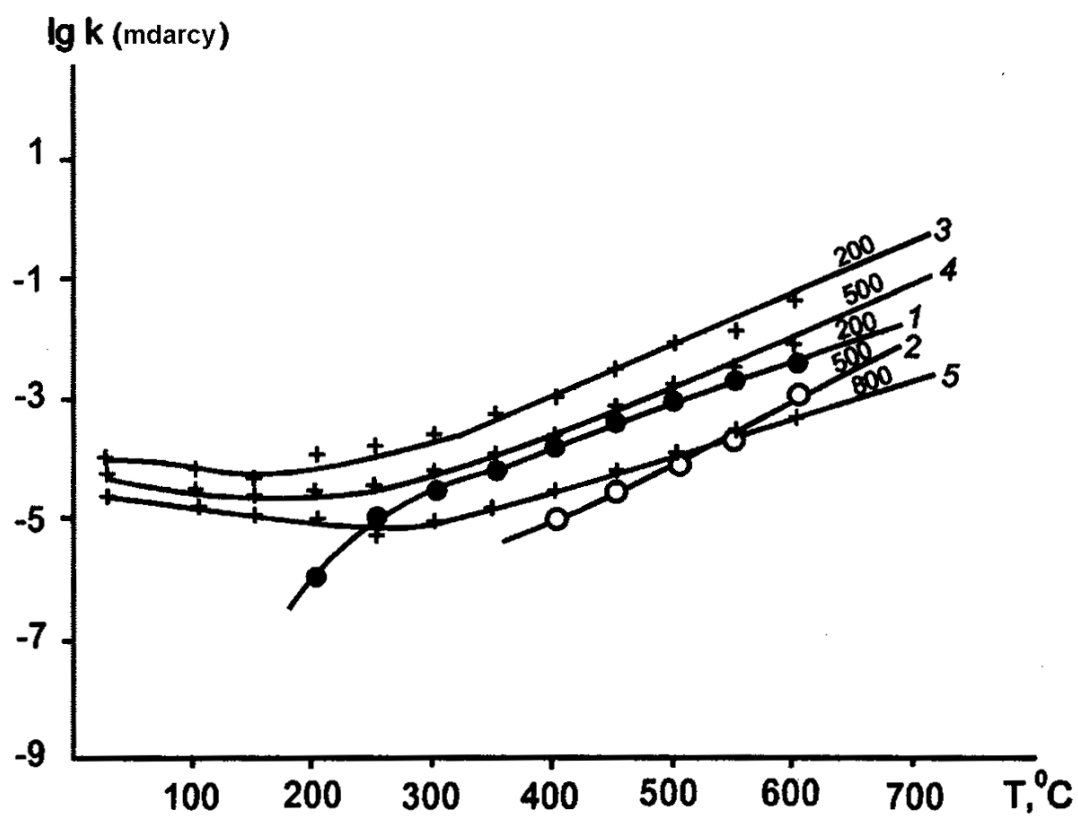


Fig.2.4 Dependence of permeability coefficients (k , millidarcys) upon temperature for various models of granites at various effective pressures.

Experimental data of V.H.Balashov and G.P.Zaraisky [1989] 1,3 – 200 bar, 2,4 – 500 bar, 5 – 800 bar.

Chapter 3

Dynamics of Metasomatic processes

3.1. Dynamics of flows of solutions and matter in microporous environment.

In the study of metasomatic processes the manner of matter transfers by solutions, as already underscored, has a fundamental significance. We distinguish diffusion metasomatism, in which the diffusion speed of components (u^{inf}) is greater than the solution's infiltration speed, and consequently, the matter transfer proceeds through the difference between the chemical potentials of components in the solutions, naturally beside the smallest value of the component's chemical potentials:

$$I^{\text{dif}} = \sum_a^k I_a^{\text{dif}} = - \sum_a^k L_a^{\text{dif}} \cdot \nabla \mu_a \quad (3.1)$$

where I_a^{dif} are the components' flows, $\nabla \mu_a \dots \nabla \mu_k$ are the gradients of the chemical potentials, $L_a^{\text{dif}} \dots L_k^{\text{dif}}$ are the linear coefficients of proportionality:

$$L_a^{\text{dif}} = \frac{I_a}{\nabla \mu_a}, \dots, L_k^{\text{dif}} = \frac{I_k}{\nabla \mu_k} \quad (3.2)$$

It is natural to express the specific flows of components by means of the transfer speed. Evidently, the speed of the general flow in case of diffusion in the same direction will be:

$$u^S = u^{\text{dif}} + u^{\text{inf}} \quad (3.3)$$

whereas in the case of contrary diffusion the general flow:

$$u^S = u^{\text{dif}} - u^{\text{inf}} \quad (3.4)$$

which only makes sense if $u^{\text{dif}} > u^{\text{inf}}$.

We demonstrate below the real significance of the speed and parameters on the basis of experimental and calculated data.

Diffusion usually proceeds individually for each component, consisting of a cooperative complex movement almost always determined by diffusion of big molecules.

In infiltration metasomatism are carried out many variants of matter transfer amongst which it is possible to distinguish two main manners: a) The

simplest case, when components' transfer occurs in the course of dissolution simultaneously with it. b) The second, most general case when each filtrating component has its own individual speed.

If we designate the filtration speed of the components from $\underline{a}$ to $\underline{k}$ through $\omega_a, \dots, \omega_k$, and the filtration speed of the dissolution through ω_0 , we can obtain the relation $\varphi_i = \frac{\omega_i}{\omega_0}$ (3.5)-which is the coefficient of filtration effect, characterizing the filtration speed of the given component relatively to the solvent.

The notion of filtration effect was introduced into geological literature by D.S.Korzhinsky (1947), who generalized the marked cases of limited permeability of the rocks [McKay, 1946]. Nature and size of the filtration effect and its role in hydrothermal and metallogenic processes present interesting geochemical problems. Theoretical and experimental research in these directions was performed, notably by the author and his collaborators [Zharikov, 1965, 1969; Zharikov & Alexin, 1971 a,b, 1973; Zharikov *et al.*, 1973; Alexin *et al.*, 1982; Experimental problems of geology, 1986 ; Experiment in solving current problems of geology, 1994].

The physico-chemical nature of the filtration effect will be examined in more detail below, its decisive role in the evolution of endogenic postmagmatic processes, including metallogenic ones. Here, without examining causes, we emphasize the component's relative speed through coefficient φ_a of the filtration effect and introduce a few main relations.

Suppose an isolated cross-section ($q=1$) through which whatever component i infiltrates:

$$dm_i = C_i W_i dt = \varphi_i \omega_0 C_i dt \quad (3.6)$$

Differentiating both members according to distance and reorganizing them we get

$\frac{1}{W_i} \cdot \frac{\partial C_i}{\partial t} + \varphi_i \frac{\partial C_i}{\partial x} + C_i \frac{\partial \varphi_i}{\partial x} = 0$ (3.7) is the filtration equation of the component i in the conditions of the varying filtration effect.

A few consequences:

a) Starting with C_i constant and $\frac{\partial C_i}{\partial x} = 0$, from (3.7) we get:

$$\frac{\partial C_i}{\partial t} = -\omega_0 C_i \frac{\partial \varphi_i}{\partial x} \quad (3.8)$$

$$\text{or } \frac{\partial \ln C_i}{\partial t} = -\omega_0 \frac{\partial \varphi_i}{\partial x} \quad (3.9)$$

from which it evidently follows that a diminution of the coefficient of the filtration effect !!!($\frac{\partial \varphi_i}{\partial x} = 0$) brings about the component “ i ” concentration in the solution flow's that will be higher in proportion of the component's initial concentration (C_i), and a significant diminution of φ_i .

b) We may suppose that surrounding rock has a somewhat constant coefficient of filtration effect, then will be reached the stationary state ($\frac{\partial C_i}{\partial x}=0$), for which:

$$\varphi_i \frac{\partial C_i}{\partial x} + C_i \frac{\partial \varphi_i}{\partial x} = 0 \quad (3.10)$$

$$\text{or } \frac{\partial(\varphi_i C_i)}{\partial x} = 0 \text{ and } C_i \varphi_i = \text{const.} \quad (3.11)$$

Equation (3.11) can be conveniently presented in the form:

$$C_i W_i = C_i^0 \omega_0 \quad (3.12)$$

where C_i^0 is the concentration for $\varphi_i = 1$ or for $\omega_i = \omega_0$.

There follows from equations (3.11) and (3.12) that in environments with different φ_i , the component's distinct concentration is established in the solution, which may exceed the saturation concentration, resulting in the corresponding components' precipitation from the solution.

Leaving aside other manifestations of the filtration effect, we underline that φ_i may be more than unity, reflecting possible variations of the hydrothermal differentiation of postmagmatic solutions.

Filtration effect usually implies the components' movement in a homogeneous liquid or super-critical solution. This however is not without fail. In general conditions the component's displacement is foreseen in the general flow of the fluid, which may be homogeneous and heterogeneous. The problem of the relative role of transfer in gaseous or liquid phase, of the metallogenetic significance of gaseous or liquid transfer, is being discussed by geologists and geochemists, notably acutely between K. Fenner, N. Bowen, V. Lindgren, K. Ross and others relatively to the role of a gaseous or liquid component in the processes of hydrothermal ore formation.

Nowadays the problem attracts special attention again, with the possibility of the components' simultaneous differential transfer by the heterogeneous gas-liquid fluids: this phenomenon's physico-chemical preconditions depend on the limited solubility in $\text{H}_2\text{O}-\text{CO}_2$ and $\text{H}_2\text{O}-\text{CO}_2$ chloride systems by means of very simple examples of hydrothermal solutions, or in the more complicated systems: $\text{H}_2\text{O}-\text{CO}_2$ -albite, $\text{H}_2\text{O}-\text{CO}_2$ -granite, $\text{H}_2\text{O}-\text{CO}_2$ -NaCl-albite and others. One of those conditions is the problem of simultaneous filtration of the heterogeneous mixture of a steam-liquid in ultraporous rocks. Experimental data in that direction are isolated. S.M. Koshenchuk [Koshentchuk, 1993] has made a series of tests on filtration of water-gas mixtures: $\text{H}_2\text{O}-\text{CO}_2$, $\text{H}_2\text{O}-\text{Ar}$, $\text{H}_2\text{O}-\text{CO}_2-\text{Ar}$ through various ultraporous filters under various pressures; main conclusion: precise information from the experiments regards the different displacement speeds in gaseous and liquid phases depending on the permeability of the environment. For a high permeability ($k=3-10$ millidarcys), the flow of the gas-water mixture proceeds in

“barbotage”; for k between $3 \cdot 10^{-6}$ and 3.0 millidarcys there occurs a homogeneous flow and finally for small permeability with $k = n \cdot 10^{-6}$ to $n \cdot 10^{-4}$ millidarcys, water dominates the flow of initial gas-water mixture. The outlined dependence requires further theoretical and experimental research.

V.M. Shmonov, V.I. Vitovtova, A.V. Zharikov and others, [Vitovtova & Shmonov, 1982; Shmonov *et al.*, 1995; Vitovtova, 1989; Zharikov *et al.*, 1993] have undertaken experimental researches on permeability of various rocks (limestone, marbles, granites, crystalline, schists, etc) at high temperatures. The influence of the rocks’ thermal plasticity on their permeability has been particularly studied [Balashov & Zaraysky, 1989; Zaraysky & Balashov, 1995].

As a result, it has been possible to distinguish various types of evolution of porosity depending on temperature, general and effective pressure, on mineralogical composition of the rocks and a few more parameters. Calculation of the evolution of the field of permeability has been attempted on a few objects: the skarn deposits of Saiak I and Tactau; the deposits of Ak-Chatau, some horizons of very deep bore holes of Kola [Vitovtova *et al.*, 1983; Zharikov *et al.*, 1985, 1990]. Referring the reader to the interesting data of these works we note some important regularities, illustrating them with diagrams (fig.3.1), building upon the results of those works.

Note that a reheating (under pressure, naturally) brings about on the whole compression and increase of permeability of the rocks. It develops in differences in lengthening of various minerals in different crystallographic directions. Naturally, this is especially marked on polymineral rocks (such as granites). Note the complex influence of temperature and effective pressure. However, as shown by experiments of V.M.Shmonov and his team, each rock type has its own gamut of non-permeability when permeability coefficients are at less than 10^{-5} millidarcys, which practically rules out a noticeable transfer of the solution.⁴¹⁾

We have shown above some important particularities in the solutions’ behavior in ultraporous environments. As shown by more thorough research it would seem that a simple process of flow of solutions in ultraporous environments develops as a complex physico-chemical phenomenon. It can be said that the conditions at the limits depend upon contrary parameters. 1) The formation of oversaturated solutions (with $P_S > P_F$) brings about filling of voids, great pores, microcracks. There follows formation of active pores of optimal dimensions, whose size is offset by necessary concentration of coexisting fluids. The processes contribute to the rocks’ thermal plasticity. 2) On the other hand,

⁴¹⁾ Remember that in thermodynamics effective pressure means difference between pressure on the rock and pressure on the fluid $P_{\text{eff}} = P_S - \alpha P_F$ where α is a coefficient that informs about general pressure on “depth”, for the condition of the earth crust α nears 1. However, for permeability, or more precisely for the flow’s speed, the fluid pressure’s gradient is extremely significant, as shown by Darcy’s law, $v = (k/\eta) \cdot (\nabla p / \nabla x)$, where v is the filtration speed, k the coefficient of permeability and η the viscosity.

the relation between *temperature and effective pressure* shows that there exist maximal dimensions of porosity, in the order of 10^{-5} - 10^{-6} millidarcys; for smaller pores the solutions' flow cannot happen; one can only invoke diffusion processes, complicated by the influence of superficial minerals.

In conclusion, the amounts of permeability of metasomatic skarns (cf. fig. 3.1), greisens and others show that their remaining permeability is sufficiently high ($n \cdot 10^{-4}$ millidarcys).

3.2. Causes and fundamental equations of metasomatism.

Metasomatism appears as a violation of the equilibrium between the surrounding rocks and coexisting hydrothermal solutions. In nature two extreme cases may be distinguished: simple and full metasomatism.

Simple metasomatism occurs when there is deviation from equilibrium during gradual evolution of the coexisting solution due to a variation of temperature (and of whatever component's solubility), a variation of the coefficient of the filtration effect (and of the corresponding concentration of any component), or the variation of other isolated factors. In that case, at the limit, variation of whatever factor results in an "isolated" act of metasomatism. Many examples of it are widely known: microclinization or albitization of feldspars through "autometasomatism" of granititoids and other rocks.

The second, extreme, case, complete metasomatism, occurs when the rock penetrates a solution the composition of which is completely independent from that of the surrounding rock. In this case the altered rocks undergo reiterated reactions with the acting solutions, with formation of a series of zones built of metasomatic minerals. The succession of zones is called metasomatic column, the regular structure of which will be examined below.

We have so far mainly considered that formation of metasomatic bodies, their structure, strength and other important peculiarities result from matter transfer through solutions. We have distinguished, accordingly, diffusion and infiltration metasomatism. The former proceeds as a rule in isothermal conditions, since the size of microporosity coefficients is usually 1.5 to 2 times higher than that of the diffusion coefficients. However, in diffusion metasomatic formations are observed regressive metasomatic transformations due to lowering temperature during the process. These changes are as a rule visible in the form of separate simple parts of metasomatic transformations.

Much more complex is the influence of temperature on infiltration metasomatic formations. These frequently seize great masses of rocks which may settle in various temperature conditions. One of the widespread and relatively simple situations occurs with the existence of a field of temperature gradient, for instance, in contact zones or apical parts of an intrusive massif. Other examples can be found of "extended" temperature fields. Also characteristic of infiltration metasomatism is temperature variation in time; but

in most cases this appears in simple metasomatic replacement, partial or total, of separate minerals; and considering the general regularity of metasomatism, these “applications” may be considered as additional complications.

As shown above, metasomatism occurs as a rule in local equilibrium, i.e. when, as against global changes of defiant metasomatic parameters, stable equilibrium occurs at each instant within whatever elementary part. However, in some metasomatites, little deep and usually of low temperature, stable equilibrium is not reached, witness the conservation of relicts of incompletely replaced minerals, conservation of parts of the rocks untouched by metasomatism and so on. In such cases, in order to examine the general structure regularities of metasomatic bodies, it is necessary either to take into account parameters linked with the kinetics of corresponding replacement reactions, or artificially to separate from the general system its part in equilibrium. But “it is an ill wind that blows nobody good”, if metasomatism always happened in total equilibrium we never could succeed in observing the finenesses of the replacement processes, the mechanism of the minerals’ reactions and so on.

In establishing a metasomatism model called theory of metasomatic zoning the method of D.S.Korzhinsky [Korzhinsky, 1951_{1,2}, 1952_{1,2}, 1953, 1969] has surely proved the most rational. This method consists in establishing and researching the simplest models of metasomatism with ulterior introduction of complements to more simple schemes reflecting more complex cases.

Besides, it is interesting to take the most general view of the problem in order correctly to evaluate the importance and limits of manifestation or predominance of some separate, constitutive, complex metasomatic processes. This has partially been made as to the common development of infiltration and diffusion metasomatism [Zharikov, 1965].

Let us examine the most general case. A solution of arbitrary composition penetrates a rock however composed in a field with a temperature gradient. If we examine any elementary volume containing rocks, the general matter flowing through this volume will naturally sum up the flows produced by certain applied forces. These flows may put together, i.e. appear as the sum of different flows, if the expression of the acting forces is correctly selected. It can be affirmed [Zharikov, 1961, 1976; see for more details the courses of irreversible thermodynamics] that there will exist between the flows linear relations if the acting forces are expressed in conformity with the equation of the growth speed of the entropy (see below).

So, the general flow may be expressed as

$$I^S = I^{\text{inf}} + I^{\text{dif}} + I^{\text{VT}} + I^{\text{kin}} \quad (3.13)$$

and for a component “i”:

$$I_i^S = I_i^{\text{inf}} + I_i^{\text{dif}} + I_i^{\text{VT}} + I_i^{\text{kin}} \quad (3.14)$$

$$\text{where } I_i^{\Sigma} = \left(\frac{dmi}{dt} \right)^S \quad (3.15)$$

I_i^{inf} being the infiltration flow, I_i^{dif} the diffusion flow, $I_i^{\nabla T}$ the flow due to temperature variation, I_i^{kin} the one influenced by the kinetics (speed) of reactions. Let us take, according to Onsager's principle

$$I_i = L_i X_i \quad (3.16)$$

where L_i is the transfer's linear coefficient and X_i the acting force, we get the general relation

$$I_i^{\Sigma} = L_i^{\text{inf}} X_i^{\text{inf}} + L_i^{\text{dif}} X_i^{\text{dif}} + L_i^{\nabla T} X_i^{\nabla T} + L_i^{\text{kin}} X_i^{\text{kin}} \quad (3.17)$$

or

$$\left(\frac{dm}{dt} \right)_i^{\Sigma} = \left(\frac{dm}{dt} \right)_i^{\text{inf}} + \left(\frac{dm}{dt} \right)_i^{\text{dif}} + \left(\frac{dm}{dt} \right)_i^{\nabla T} + \left(\frac{dm}{dt} \right)_i^{\text{kin}} \quad (3.18)$$

The expression of the acting forces in general form is obtained from the equation of the growth speed of the entropy (De Groot & Mazur, 1964; Zharikov, 1965, 1976) :

$$\frac{d_i S^u}{dt} = -\frac{1}{T} \left(\frac{d_i U}{dt} \right) = -\nabla \frac{1}{T} \cdot \frac{dQ}{dt} + \nabla \frac{p}{T} \cdot \frac{dV}{dt} - \sum_a^k \nabla \frac{\mu_a}{T} \cdot \frac{dm_a}{dt} \quad (3.19)$$

where $\frac{d_i S^u}{dt}$ is the growth speed of the entropy in the irreversible process in the system $U = f(S, V, m_a \dots m_k)$. One can be sure that a similar expression of irreversible changes through the system's thermodynamic potentials can be obtained for any thermodynamic system, including those with perfectly mobile components [Zharikov, 1976].

Then the general equation of the matter transfer (of the component i) for the metasomatism may be expressed as

$$I_i^S = L_i^{\text{inf}} \cdot \nabla \frac{p}{T} - L_i^{\text{dif}} \cdot \nabla \frac{\mu_i}{T} + L_i^{\nabla T} \cdot \nabla \frac{1}{T} - L_i^{\text{kin}} \cdot \nabla \frac{\mu_i}{T} \quad (3.20)$$

Note that Onsager's principles, law of linear correlation and reciprocating principle, establishing a correlation between different processes simultaneously flowing in the system are correct only for a selection of flow and acting forces which conforms to the equation of growth speed of the entropy in the system (equation 3.19), as made in equation 3.20.

The general flow equation (3.20) is at the basis of the conclusion of the equation of metasomatic zoning. However, the conclusion of the generalized equation of metasomatic zoning is so important that it is certainly more reasonable first to deduce an equation of the separate types of metasomatism and then, remembering the corresponding selection of active forces, to add the real flows. It is also useful, in order to simplify the operations, to consider that in the framework of one dimension space. In order to underscore the important ideas and conclusions we have omitted many indispensable calculations, referring the reader for details to specialized works.

3.3. Metasomatic zoning of isothermic infiltration

Conclusion of the equation of zoning of isothermic infiltration

In equation (3.20), the infiltration flow through a single volume of the component “i” is defined as

$$I_i^{\text{inf}} = \left(\frac{dm_i}{dt} \right)^{\text{inf}} = L_i^{\text{inf}} \cdot \frac{\nabla P}{T} \quad (3.21)$$

In isothermic conditions we have $\frac{L_i^{\text{inf}}}{T} = L_i^{\text{inf}}$; for a one-dimensional flow through an isolated section, ∇p changes into $\frac{\partial p}{\partial x}$, then:

$$\left(\frac{dm_i}{dt} \right)^{\text{inf}} = L_i^{\text{inf}} \left(\frac{\partial p}{\partial x} \right) \quad (3.22)$$

In equation (3.22) L_i^{inf} expresses the unity quantity of component “i” moving through the flow, and $L_i^{\text{inf}} = \varphi_i C_i$ (3.23), where C_i is the component’s concentration in the solution and φ_i the coefficient of the filtration effect. In accordance with the known equation of the hydrodynamic speed of filtration one gets the equality:

$$v = \frac{k}{\eta} \cdot \frac{\nabla p}{\nabla l} \quad (3.24)$$

where η is the solution viscosity, k is the coefficient reflecting the structure (permeability) of the surroundings, and $\frac{\nabla p}{\nabla l}$ is the “hydraulic gradient”, none other than the pressure gradient for the one-dimensional flow equal to $\frac{\partial p}{\partial x}$. Then, designating the filtration speed of the given solution in the given surroundings by ω_0 , we get:

$$\omega_0 = \frac{v \cdot \eta}{k} = \frac{\nabla p}{\nabla l} \quad \text{and} \quad \omega_0 = \frac{\partial p}{\partial x} \quad (3.25)$$

Finally, the filtration equation of component “i” through a single section is noted as

$$dm_i = \varphi_i \cdot C_i \cdot \omega_0 \cdot dt = \varphi_i \cdot C_i \cdot dv \quad (3.26)$$

where v is the volume of the infiltrating solution $dv = \omega_0 \cdot dt$.

The equation (3.26) has been used by D.S.Korzhinsky [1969] as a conclusion to the equation of infiltrating isothermal metasomatic zoning.

Admittedly, the rock's composition is arbitrary, but homogeneous; the solution's composition is arbitrary, but constant, unchanging in time; the system of pores is uniform, but insignificant, i.e. the rock's volume remains constant; so does the temperature as stipulated. The principle of local equilibrium is observed.

Starting from equation (3.26) we derive according to distance x and anticipatively reassemble the two members: $\frac{\partial\left(\frac{dm_i}{dv}\right)}{\partial x} = \frac{\partial(\varphi_i C_i)}{\partial x}$, and as a result we get the expression

$$-\frac{\partial i}{\partial v} = \varphi_i \frac{\partial C_i}{\partial x} \quad (3.27)$$

which shows that by infiltration of an elementary volume of the solution ∂v into an elementary volume of solid rock (a volume delimited by a single section shifting along the elementary distance ∂x), there occurs a linked change in the component i 's content in the solid rock (∂i) and in the concentration (C_i) of the same component in the infiltrated solution. The sign minus signifies the inverted order of the difference from initial to final state, φ_i ; the coefficient of the filtration effect is taken as constant; we neglect the content of component i in the porous solution. If the later is important, the expression (3.27) takes the form:

$$-\left(\frac{\partial i^s}{\partial v} + \frac{\partial i^p}{\partial v}\right) = \varphi_i \frac{\partial C_i}{\partial x} \quad (3.28)$$

$$\text{Or } -\left(\frac{\partial i^s}{\partial v V} + \rho \frac{\partial C_i}{\partial v}\right) = l_i \frac{\partial C_i}{\partial x} \quad (3.28a)$$

where ρ is the initial porosity (volume of pores) of the initial rock. Taking the pores volume into account has meaning in particular cases; generally this member may be neglected.

If the solution contains an arbitrary number of components " k ", it is natural to have " k " equations like (3.27):

$$\frac{\partial a}{\partial v} = \varphi_a \frac{\partial C_a}{\partial x}, \dots; \quad -\frac{\partial i}{\partial v} = \varphi_i \frac{\partial C_i}{\partial x}; \quad -\frac{\partial k}{\partial v} = -\varphi_k \frac{\partial C_k}{\partial x} \quad (3.29)$$

We recall the condition that the process must develop in local equilibrium, i.e. each moment in each elementary volume defined by the size of components' content in the solid rock, corresponds a single concentration in equilibrium of those components in the solution. Thus, there are in all equations only two independent parameters, the direction x and the volume v of the infiltrating solution. In this case, the variation of content of any component " i " is identically expressed as:

$$d_i = \left(\frac{\partial i}{\partial v} \right)_x dv + \left(\frac{\partial v}{\partial x} \right)_v dx$$

(3.30)

and if one chooses any section with a constant content “ i ”, i.e. $d_i = 0$, equation (3.30) can take the form:

$$\frac{dx}{dv} = - \frac{\left(\frac{\partial i}{\partial v} \right)}{\left(\frac{\partial i}{\partial x} \right)}$$

(3.31)

Comparing (3.31) with (3.27) we easily obtain:

$$\left(\frac{dx}{dv} \right)_i = \varphi_i \frac{\partial C_i}{\partial x} \div \frac{\partial i}{\partial x}$$

(3.32)

where $\frac{dx}{dv}$ is the relative displacement speed of the section with constant concentration “ i ” in dependence upon change of concentration and content of component “ i ” along an elementary segment of the path of the infiltrating solution.

Obviously, such an expression of relative speed can be obtained for all the “ k ” components, and we have a system of “ k ” equations in the form of (3.32):

$$\begin{aligned} \left(\frac{dx}{dv} \right)_a &= \varphi_a \frac{\partial C_a}{\partial x} \div \frac{\partial a}{\partial x} \\ \left(\frac{dx}{dv} \right)_i &= \varphi_i \frac{\partial C_i}{\partial x} \div \frac{\partial i}{\partial x} \\ \left(\frac{dx}{dv} \right)_k &= \varphi_k \frac{\partial C_k}{\partial x} \div \frac{\partial k}{\partial x} \end{aligned}$$

(3.33)

In the system (3.33) the two variables x and v can be replaced by one variable $\frac{x}{v}$ or $\frac{dx}{dv} = u$, expressing relative speed. In which case system (3.33) may be replaced by one equation:

$$u^{\text{inf}} = \left(\frac{dx}{dv} \right)_{a..k} = \varphi_a \frac{dC_a}{da} = \dots = \varphi_i \frac{dC_i}{di} = \varphi_k \frac{dC_k}{dk}$$

(3.34)

that expresses the dependence of the transfer speed of the column’s section upon the components’ concentration change in the solution and their content in the rock.

Equation (3.34) also shows that if we have chosen a determined section after any physical index for any component (constant content of

component “ i ”) the chosen section behaves in the same way for all other components. If in this section there occurs a change $\frac{dC_i}{di}$ for any component i there will occur in this section a change in concentration and content of all other components (another possible solution can only give an indetermination $\frac{0}{0}$).

If in the chosen section final changes occur in content and concentration of the components, equation (3.34) should be written in the form:

$$u^{\text{inf}} = \frac{x}{v} = \varphi_a \frac{\Delta C_a}{\Delta a} = \dots = \varphi_i \frac{\Delta C_i}{\Delta i} = \varphi_k \frac{\Delta C_k}{\Delta k} \quad (3.35)$$

Equations (3.34) and (3.35) are called equations of isothermal metasomatic infiltration zoning, or of isothermal metasomatic infiltration column. Further consideration will demonstrate this denomination’s legitimacy. Note that solving equations (3.34) and (3.35) has require some indispensable mathematical subtleties; a discussion of these details as can be found in the works of D.S. Korzhinsky [1969, 1973], P. Lichtner [Lichtner, 1991], and B. Guy [Guy, 1993].

Let us now examine the properties of infiltration of metasomatic zoning resulting from equations (3.33) and (3.34). Surprising is the concordance between these particular properties and of composition and structure of natural metasomatites and experimental metasomatic columns; it undoubtedly serves to a direct demonstration of the validity of the conclusion adduced above.

General properties of the isothermal infiltration metasomatic zoning

We propound this part somewhat differently from D.S.Korzhinsky (1951), though rigorously following his main principles.

1. The cause of arising of a section consists in the replacement of minerals by one another (at the limit of one by another). In fact, C_i in equations (3.34) and (3.35) represents saturation concentration of a given component according to a given determined mineralogical composition of the rock. Saturation concentration is invariable for a constant composition of the rock, because any compatible concentration variation occurs at the limit with an infinite speed $\left(\frac{\Delta C_i}{\Delta i} = \frac{\Delta C_i}{0} = \infty\right)$. That is why the only cause of appearance of a section is the appearance of a replacement front with qualitative change of the mineralogical composition, i.e. appearance of new minerals replacing the initial association. Then equations (3.34) and (3.35) describe corresponding fronts of exchange with minerals of constant composition, where:

$$u^{\text{inf}} = \frac{x}{v} = \varphi_a \frac{\Delta C_a}{\Delta a} = \dots = \varphi_i \frac{\Delta C_i}{\Delta i} = \varphi_k \Delta \frac{\Delta C_k}{k} \quad (3.35)$$

ΔC_a and $\Delta i \dots \Delta C_k$, Δk point to variation of concentration and content of the components in any such section or, better, at each replacement front. Thus, evidently, the higher $\frac{\Delta C_i}{\Delta i}$ the higher the corresponding displacement speed ($\frac{x}{v}$) of such a section.

A few useful graphs will illustrate these relations. We take for example a column with three replacement fronts $\left(\frac{x}{v}\right)^{\text{I}} > \left(\frac{x}{v}\right)^{\text{II}} > \left(\frac{x}{v}\right)^{\text{III}}$, then on the diagram $x - v$ (fig. 3.2a) one can observe three straight lines $\left(\frac{dx}{dv}\right)^{\text{I}} = \text{tg } \alpha_1 > \left(\frac{dx}{dv}\right)^{\text{II}} = \text{tg } \alpha_2 > \left(\frac{dx}{dv}\right)^{\text{III}} = \text{tg } \alpha_3$, representing relative transfer speed corresponding to the replacement fronts. Figure 3.2b shows diagram $C_i - i$ of intrusion and removal of component “i”, where the slant lines characterize the relation to the transfer speed of the section, but at a fixed point the content and concentration of component “i” between the sections, i.e. in the metasomatic zones.

2. The sharp replacement limits and the constant composition of the minerals and the solution at the limits of the zones appear as the characteristic graph of the isothermal infiltration metasomatism. This conclusion is well visible in metasomatites formed by minerals of constant composition. In fact, if $C_a \dots C_k$ are the saturation concentrations in equilibrium with associated minerals of constant composition, they remain constant in the limits coexisting with this association, i.e. the limits of the metasomatic zone. The zone’s mineral composition also remains constant in so far as the saturation concentration does not depend upon the quantity of minerals and, on the contrary, the variations in quantitative correspondence would lead to variation of concentration of the coexisting solution.

Variation $C_a \dots C_k$ may be only linked with variation in the zone’s mineralogical composition, or, as may be said, to the qualitative variation of the mineralogical composition, which occurs with the formation of a replacement front of some minerals by others. In local equilibrium this front will be sharp: to the percolation of each elementary volume of solution corresponds elementary replacement of some minerals by others, with corresponding variation of concentration and content of the component which in local equilibrium occurs much more rapidly than the solution’s infiltration.

If along the column with minerals of constant composition, this regime replacement is sufficiently clear and no special demonstrations are needed, except reducing ones; then not so evident is analogous constancy of

concentration and composition of the rock, with sharp replacing fronts for metasomatic zones with minerals of variable composition. An elegant demonstration of this has been made by D.S.Korzhinsky. We summarize it, referring for details to the original [D.S.Korzhinsky, 1969].

On fig. 3.3 is represented the diagram of concentration (C_i), (i) content of component “ i ”, in which there is the components i ’s content in minerals of variable composition $M(M_1-M_2)$, $N(N_1-N_2)$ and $P(P_1-P_2)$ and the curve of relation C_i-I for these minerals (remember that for minerals of variable composition we always have $\frac{\partial \mu_i}{\partial x_i} > 0$, hence $\frac{\partial C_i}{\partial i} > 0$). Finally on the diagram

are plotted the lines corresponding to sections $\left(\frac{x}{v}\right)^I > \left(\frac{x}{v}\right)^{II} > \left(\frac{x}{v}\right)^{III}$, where

$\frac{x}{v} = \varphi_i \frac{\Delta C_i}{\Delta i} = \varphi_i \tan \alpha$, on which occurs replacement of minerals with one another, with intrusion of component “ i ” (line **a**) and its removal (line **b**) (φ_i , naturally, constant).

It can easily be seen that the lines of the replacement fronts coincide only with definite constant compositions of minerals’ solid solutions. In case of intrusion of component i , it is the combination $M_2 | N_2 | P_2$ that traces, in Roman figures, the replacement fronts. In case of removal it is the combination are $P_1 | N_1 | M_1$. These correlations clearly show that the minerals’ solids solutions in the isothermal infiltration columns possess a constant composition and that only in certain cases is possible a very limited change of composition; for the column of removal there are the minerals N_1 and M_1 , whose possible change of composition is indicated on fig.3.3 by a vertical dotted line.

In this way and in that case, when metasomatites accumulate minerals of variable composition, the composition of minerals and solutions at zone limits remain constant and replacement occurs suddenly there. Thus, (cf. fig. 3.3) such and such a mineral can be replaced with a sudden variation of its composition: $M_1 | M_2 | N_2 | P_2$.

Thus, constancy of composition of minerals and solutions at zone limits and sudden, jerky variation at those limits are characteristic features of isothermal infiltration metasomatoses.

Another important feature is indicated on the diagram. There occurs in infiltration metasomatoses in each zone a maximal concentration of intruding and a minimal one of removal components from those possible, compatible with the given mineral composition of the zone. This immediately follows from

equation (3.35) $\frac{x}{v} = \varphi_i \frac{\Delta C_i}{\Delta i}$. If Δi is constant, $\frac{x}{v}$ is as much higher as

the difference of concentration C_i is greater. At the zones’ limits $\Delta i = 0$ and $\frac{\Delta C_i}{\Delta i}$

$= \infty$, i.e. the component's concentration attains infinitely quickly maximal or minimal values, compatible with the given mineral composition.

It also follows from equation (3.34) and (3.35) that the relative distance between sections, in other words, the interval between metasomatic zones,

$$\frac{l}{v} = \left(\frac{x}{v}\right)^I - \left(\frac{x}{v}\right)^{II} = \varphi_i \left[\left(\frac{\Delta C_i}{\Delta i}\right)^I - \left(\frac{\Delta C_i}{\Delta i}\right)^{II} \right] \quad (3.36)$$

depends upon the components' variations in concentration and composition at the limits of the zone of the replacement front.

3. Metasomatic column and the cause of metasomatic zoning.

Equation (3.34) $\left(\frac{dx}{dv}\right) = \varphi_a \frac{dC_a}{da} = \dots = \varphi_i \frac{dC_i}{di} = \varphi_k \frac{dC_k}{dk}$ defines the limit

(replacement front) between two metasomatic zones. If each zone contains "k" components the general number $2k$ of parameters will be linked by $(k-1)$ equations of the form (3.34) and the number of independent parameters for two contiguous zones will be $2k - (k-1) = k+1$. If the initial rock contains k components, whose compositions naturally are independent parameters on appearance of a front or, in other words, a metasomatic zone independent from the rock's initial composition but depending therefore upon the components' concentration in the solution, there is only a single parameter. Expressed in thermodynamic parameters, it can be said that if the initial rock is determined by k contents of inert components, then on transition towards the first metasomatic zone one of the parameters becomes intensive, depending upon the concentration of the component in the influencing solution.

These constructions may be extended in keeping with the subsequent replacement fronts. So, in transition from the first metasomatic zone with $(k-1)$ contents of inert components to a subsequent zone, one more parameter, due to equation (3.34), remains intensive, depending on concentration of this component in the solution, but $(k-2)$ contents of independent components in the initial rock will be determined, i.e. will behave like inert components, etc. Provided in the general case the number of fronts is equal to k , an equal number of components will successively pass to the perfectly mobile state and the number of metasomatic zones will in the general case be equal to $Z = k + 1$ (3.37). This cluster of simultaneously formal zones is called *metasomatic column*.

D.S. Korzhinsky's introduction of the notion of metasomatic column into scientific usage was the chief novelty in the explanation of metasomatic processes. We insist on this. The zonal structure of the metasomatic aureole had long been known to geologists and zoning was always considered as resulting from some metasomatites succeeding to others. This was

a natural interpretation of observations of metasomatites replacing one another and was linked to variation in the composition of the active solution. There was no attempt whatever at expressing these presentations in the form of a mutual coordination model.

D.S. Korzhinsky's physico-chemical model has shown that exactly on the contrary, in the most general case, i.e. for an arbitrary independent composition of the initial rocks and the influencing solution, a metasomatic column must arise as aggregate of metasomatic strictly limited zones, formed simultaneously.

The cause of metasomatic zoning is the components' differential mobility, i.e. their successive passage from inert state to perfect mobility, creates replacement fronts that form a column of metasomatic zones of different mineral composition.

It is well known that the number of minerals is defined by that of the system's extensive parameters, and in the case of metasomatism $r_{T,V,\mu}^{\max} = k_i + 1$, i.e. equals the number of inert components in plus the volume. The successive passage of components from the inert to the perfectly mobile state produces a corresponding diminution of the number of minerals in the zones of the metasomatic column up to the last monomineral rear zone, formed under the perfectly mobile behavior of all components. The volume occupying this zone is filled by a mineral in connection with the components the solution of which is most saturated and which consequently develop the highest crystallization pressure.

Decrease of the minerals' number in the metasomatic zones through increasing intensity of the process up to formation of monomineral zones is a most characteristic, distinctive feature of metasomatic processes.

In order to understand a metasomatic column as aggregate of simultaneously formed of zones, the question arises what "simultaneous" means in the physical expression and what are the real dimensions of these initial zones and columns. Computerized modeling has shown that the unstable state (when equation (3.37) and (3.35) do not function and there is no local equilibrium), represents a negligible small part of the initial time. So, experiments show [Zaraisky, 1989] that in simple column (with few zones) for a column thickness of 0.3 to 0.4 mm, all the zones are clearly seen under the microscope, the limits are sharp, with no mineral relicts. The formation time of an experimental column is always known; it depends upon the initial rock's composition, upon the solution's composition and concentration and of course upon temperature. Considering average numbers, at high temperatures (400-500°C) a column is 2.0 to 5 mm thick and requires 144 to 216 hours. In other words, the mobility speed of the front of the constituted column is in round numbers 0.3 to 0.6 mm per day or 108 to 216 mm per year. Taking porosity in natural environments to be substantially smaller (20 to 30 times), we can take speeds of 3.6 to 10.8 mm per

year. The usual thicknesses of the zones of infiltration metasomatic changes are at least a few meters to a decameter. In other words the “kinetic stage” lasts thousandths and even ten-thousandths of the time of the column’s formation.

Note that the succession of mineralogical reactions in the “kinetic zone” corresponds in principle to the replacement reaction in the column in local equilibrium. This is explained by the fact that the acting forces determining the replacement front’s transfer speed prove in principle the selfsame that determine the speeds of replacement reactions. So, according to equations (3.34) and (3.35) the propagation speed of the replacement front in the metasomatic column is as much higher as the difference between the components’ concentration in contiguous zones is greater. Speed of the chemical reaction also depends upon the components’ concentration and, for the replacement reactions, is so much higher as the difference of the components’ concentration is greater. That is why the column, having arisen in the first instants as kinetic, reorganizes itself easily and rapidly in local equilibrium.

The column having formed progressively as the solutions were infiltrating undergoes only proportional increase as far as all the similar values shown in parentheses,

$$x^I = \left(\varphi_a \frac{\Delta C_a}{\Delta a} \right) v \quad \text{and} \quad l^{I/II} = x^I - x^{II} = \left[\left(\varphi_a \frac{\Delta C_a}{\Delta a} \right)^I - \left(\varphi_a \frac{\Delta C_a}{\Delta a} \right)^{II} \right] v$$

remain constant. Only the volume of the infiltrating solution is a variable independent parameter.

If the metasomatic solution contains “ k ” components, among which initially are all inert (k_i), the number (r) of zones is generally equal to $Z = k_i + 1$ (3.36), as we saw. Remember that $f_{ex} = r_{T,V,\mu}^{\max} = k_i + 1$.

This zoning, conditioned by the components’ alternative passage from inert to perfectly mobile state, is called *fundamental* (principal) *zoning*. But the sequel, in which the components reach perfect mobility, has been called *degree of components’ differential mobility* or more simply degree of components’ mobility.

The equation of infiltration zoning clearly, expresses quantitatively the causes of various differential mobility of the components. If the external replacement front is characterized by passage to the perfectly mobile state of component “a” and the following front arises owing to the change of regime of

component “b”, we evidently get: $\left(\frac{x}{v} \right)^I = \varphi_a \frac{\Delta C_a}{\Delta a} > \left(\frac{x}{v} \right)^{II} = \varphi_b \frac{\Delta C_b}{\Delta b}$. In other words, the components’ mobility depends upon the variation of concentration and the linked change of composition of the component when passing from one metasomatic zone to another: the higher the variation of concentration of the saturation at lesser change of content of the component, the more mobile will be the given component. It follows that there cannot be an “absolute” scale of

mobility. The components' mobility is defined by the composition and concentration of the influencing solution, by the composition of the replaced mining rocks. On the other hand we observe preferential inertia of ill soluble components such as Al_2O_3 or TiO_2 in many metasomatic processes.

If multizonal columns, with $Z = K_i + 1$ zones, present the most general cases of metasomatism, another extreme case is observed when under the action of definite causes a single component alters its regime or its concentration becomes different from that of the solution in equilibrium. In this case there appears only one replacement zone, without multizonal columns forming. This is called *simple metasomatosis*, as we pointed out above. Widely known examples are: postmagmatic microclinization, granite albitization and many others. Of course in natural conditions we come across various intermediary formations, from total multizonal to simple metasomatites.

Two further important features of isothermal infiltration columns are worth mentioning. Considering the "stable inertia" of some components and the diversity of composition of natural minerals, it can be surmised that, in nature also cases are repeatedly met when, on removal (or addition) of an inert component there occurs more than one reaction of the rock with the solution with formation of reaction minerals distinguished mainly by the maintenance of one inert component, for example in the scheme:

→ $\overset{\text{IV}}{A} \mid \overset{\text{III}}{A+AB} \mid \overset{\text{II}}{A+AB_2} \mid \overset{\text{I}}{A+AB_2+C} \rightarrow$ where the arrows indicate components B and C reaching the perfectly mobile state. Or the natural example of the internal zones of a greisens column:

IV	III	II	I
→ quartz	quartz + topaz	quartz + muskovite	quartz + muskovite + kalispat →
↑↓		↑↓	
Al		K	

In both columns, zones II and III contain the same number of minerals and, consequently of inert components: conditional component B in the first position column; component A1 in the second greisen column. Only, the maintenance of inert components in zones II and III is different, owing to the possibility of appearance of reactions minerals, ensuring a minimum decrease of free energy at the passage from zone to zone (see below). This type of zoning is in expediency called *complementary*. As its distinctive sign serves the identical number of minerals in the contiguous zones.

Another feature in the structure of infiltration metasomatic columns is the fact that the external zones with feeble variation, often regionally extended are formed in isobaric conditions ($r_{T,p,\mu}^{\max}=k_i$), whereas the internal zones with

strong transformations always appear in constant volume ($r_{T,V,\mu}^{\max} = k_i + 1$). There is usually in these columns $Z = K_i$ in so far as in a change of isobaric towards isochoric regime two components at once reach the perfectly mobile state. Such correlations are particularly characteristic of the zones of propylitization, beresitization and quartz-sericitic metasomatism in the coarse evolution of these processes of variations of eruptive rocks. The cause of change of the “mechanical” regime of the process is rather simple: in the external zones, where addition and removal of components are insignificant (3-4%), this is easily compensated by an even more insignificant variation of volume at formation of hydroxylate silicates, carbonates, etc. Through an intense removal of components happening in the internal zones, occurring voids are immediately filled with a deposit of a mineral of the most saturated solution. In metasomatites linked to granitoids, such a mineral is quartz, and the change from isobaric to isochoric regime proceeds by the silica passing to the perfectly mobile state. In metasomatites on basic rocks the role of perfectly mobile mineral is often played by a carbonate.

To illustrate the exposition and make it concrete we show on table 3.1 a beresitization column of acid eruptive rocks characteristic of the polymetallic deposits of Karamazar. The external zones (1, 2, 3) having a coarse extension, differ by partial rock transformations and, for many researchers, are not even linked to beresitization. This is surely false. Moreover these external transformations are specific of each type of perimetalliferous changes and may properly indicate periveinous variations. Starting from zone 4, there appear significantly more intensively transformed rocks (feldspar dissolution etc.). These transformations occur isochorically, in conditions of constant volume of the rocks, and the role of perfectly mobile mineral, filling up the volume deficit, is played by quartz. Characteristically and instructively, all reactions at the limits of zones 3/4, 4/5, 5/6, 6/7 occur by addition of silica, and quartz even replaces ankerite, pyrite, i.e. originally no maintenance of silica.

Table 3.1. Metasomatic column of beresitization

Zone of column	Zone of mineral associations	Reaction of replacements and components becoming perfectly mobile
1	Qtz ⁺ Or ⁺ Ser ⁺ Ab ⁺ Chl ⁺ Cc ⁺ Py	Or→
2	Qtz ⁺ Ser ⁺ Ab ⁺ Chl ⁺ Cc ⁺ Py	→Ab±Ser±Qtz Chl ⁺ Cc→
3	Qtz ⁺ Ser ⁺ Ab ⁺ Ank ⁺ Py	→Ank ⁺ Ser(↓↑K) Ab→
4	Qtz ⁺ Ser ⁺ Ab ⁺ Ank ⁺ Py	→Ser ⁺ Qtz(↓↑Na) ⁺ (↓↑Si) Ank→
5	Qtz ⁺ Ser ⁺ Py	→Qtz(⁺ ↓↑Mg) Py→
6	Qtz ⁺ Ser	→Qtz(⁺ ↓↑Fe) Ser→
7	Qtz	→Qtz

Increase of mobility→		Type of process
Inert components	Components perfectly mobile	
Al, Fe, Mg, Si, Na, Ca, K	O ₂ , S ₂ , CO ₂ , H ₂ O	P = const.
Al, Fe, Mg, Si, Na, Ca	K, O ₂ , S ₂ , CO ₂ , H ₂ O	
Al, Fe, Mg, Si, Na	Ca, K, O ₂ , S ₂ , CO ₂ , H ₂ O	
Al, Fe, Mg	Si, Na, Ca, K, O ₂ , S ₂ , CO ₂ , H ₂ O	V = const.
Al, Fe	Mg, Si, Na, Ca, K, O ₂ , S ₂ , CO ₂ , H ₂ O	
Al	Fe, Mg, Si, Na, Ca, K, O ₂ , S ₂ , CO ₂ , H ₂ O	
All components perfectly mobile		

4. Main conclusions. Theoretical research and experimental models, together with natural observations, show that isothermal infiltration metasomatism is characterized by the following important features:

a) Through infiltration of solutions whose composition is arbitrary but determined, unchanging in time through the rock the compositions of which is arbitrary but homogeneous and constant in space, is formed a column of sharply limited zones, differing in their own mineral composition.

b) There occurs at the zone limits a sudden, jerky change in the composition of the rock and of the solution; in the limits of the zones the compositions of rocks and solutions remain constant.

c) Replacement processes appear only at the zone limits and are expressed in exchange of minerals with minerals of another composition.

d) As solutions infiltrate there occurs only a proportional increase of the column's zones, without variation of their composition or structure.

e) Metasomatic zoning produces differential mobility of components: at each zone limit, as the infiltration process grows more intensive, a successive passage occurs of the components from inert to perfectly mobile state; this succession is called row of differential mobility of components.

f) The components' mobility is determined by their concentration in the solution and their composition in the replaced rocks; the greater the concentration variation for a lesser variation in the component's content at the replacement front (zone limit), the higher is the mobility of the given component.

g) Successive passage of components from inert to perfectly mobile state decreases the number of minerals in metasomatic zones (at the limit on one mineral at each zone limit) until monomineral rear zones are formed; decrease in the minerals' number as metasomatism intensifies and, correspondingly, the intensity of the rocks' chemical transformation remains a characteristic distinctive peculiarity of metasomatites.

h) Fundamental zoning, produced by the components' differential mobility, may be complicated by complementary zoning with the possibility of some beneficial thermodynamic reactions of rock and solution without regime change of components.

i) Evidently there is in the external zones of feeble variation the usual change from isobaric to isochoric conditions in intensive metasomatism.

The mentioned peculiarities characterize the most important properties of metasomatic infiltration zoning. They represent the general idealized model of isothermal infiltration metasomatism. Natural metasomatic columns developing in concrete geological environment, corresponding to or approaching the limit of the mentioned properties, may have their specific peculiarities. For instance, the frontal progression of a metasomatic column occurs in condition of homogenous porosity. The presence of zones of high permeability and jointing produces, naturally, primary, outstripping developments of metasomatites in these zones.

The model of infiltration metasomatism depends on the principle of local equilibrium. However, in a series of cases, particularly among metasomatites of lower temperature, owing to irregular permeability or feeble reaction speeds, mineral relicts are preserved of preceding zones. They are easily discerned by the replacement structure or by their irregular distribution. Of course, these minerals must in theoretical analysis be connected to a preceding zone. But, on the other hand, if there were no mineral relicts and if the principle of local equilibrium were absolutely applied, we never could decipher the detail of the replacement mechanism.

Finally, in the zone of metasomatic transformation by the solution can be perceived the differences with the initial rock's composition. In principle two extreme cases can here be distinguished.

In one of them, when the change of chemical composition (i.e. of the content of inert components) is small, there occurs then a variation of quantitative relations of the minerals, fixing the virtual inert components. In the other case there occurs a radical change in the initial rock's composition. Metasomatites formed on them are to be considered as an independent column: it has another structure. An instance of beresites and listvenites has been scrupulously studied, but there will be situations where these limits will be difficult to draw.

3.4. Diffusion metasomatic zoning

Conclusion of the equation of diffusion metasomatic zoning

Starting from the equation (3.20) of general matter flow for the isothermal diffusion flow of component "i" we get the expression:

$$J_i^{dif} = \left(\frac{dm_i}{dt} \right)^{dif} = -L_i^{dif} \cdot \nabla \mu_i \quad (3.38)$$

where L_i^{dif} is the kinetic coefficient expressing the quantity of component "i" percolating through a unitary section at a given temperature and a given activity of force $\nabla \mu$. For the one dimensional flow this expression may become:

$$\frac{\partial m_i}{\partial t} = -L_i^{dif} \cdot \frac{\partial \mu_i}{\partial x} = -\frac{L_i^{dif} \cdot RT}{C} \cdot \frac{\partial C}{\partial x} = -D_i \frac{\partial C_i}{\partial x} \quad (3.39)$$

or

$$\frac{\partial m_i}{\partial t} = -D_i \frac{\partial C_i}{\partial x} \quad (3.40)$$

Equation (3.40) expresses Fick's first law, also designating the quantity of component "i" percolating at each time unity through a unitary section under a concentration gradient equal to $\frac{\partial C_i}{\partial x}$. Comparing the members of equations (3.39) and (3.40), it is not difficult to see how through a complex multifactorial non-linear value it represents the well-known diffusion coefficient:

$$D_i = \frac{L_i^{dif} \cdot RT}{C_i} \quad (3.41)$$

Taking the derivative from both members of the equation:

$$\frac{\partial}{\partial x} \left(-\frac{\partial m_i}{\partial t} \right) = \frac{\partial}{\partial x} \left(D_i \cdot \frac{\partial C_i}{\partial x} \right) \quad (3.42)$$

and adopting, as above, the section as isolated, but D_i as independent of distance, one gets the expression of Fick's second law:

$$\frac{\partial i}{\partial t} = \frac{\partial}{\partial x} \cdot \left(D_i \frac{\partial C_i}{\partial x} \right) \quad (3.43)$$

where $\frac{\partial i}{\partial t}$ is the content variation of component "i" in a unity of volume of rock, and $\frac{\partial}{\partial x} \cdot \left(D_i \frac{\partial C_i}{\partial x} \right)$ its concentration variation in the solution. In (3.43) we neglect the rock's porosity with component "i"'s content in the porous solution since they are very small relatively to the general determination of the metasomatism. But if they are important, equation (3.43) should be replaced by another one:

$$\frac{\partial (i^s + \rho C_i)}{\partial t} = \frac{\partial}{\partial x} \left(D_i \frac{\partial C_i}{\partial x} \right) \quad (3.44)$$

where i^s is the content of component "i" in the solid rock, ρ the porosity (the volume of pores), C_i component "i"'s concentration in the porous solution.

Equations (3.43) and (3.44) are equivalent to the usual notation of Fick's second law:

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \cdot \left(D_i \frac{\partial C_i}{\partial x} \right) \quad (3.45)$$

The only difference is that in (3.45) $\frac{\partial C_i}{\partial t}$ refers to component i's concentration variation in the solution's unitary volume for diffusion in a homogeneous environment. For our purpose, examination of diffusion metasomatism, it is important to choose as particular symbol $\frac{\partial i}{\partial t}$, concentration variation (content in the unitary volume) in the solid rock.

If the solution contains "k" components, it is clear that we have k equations of the form (3.43), each characterizing each component's independent diffusion. Equations (3.43) to (3.45) are nonlinear and their solution for systems with several components is a difficult problem.

They usually are restricted to partial solutions (with determined limited conditions) and to allowed approximations.

Referring the reader to the original works for the necessary discussion [Korzhinsky, 1968, 1982; Frantz & Mao, 1976; Diemin & al., 1979;

Balashov, 1985, 1992; Guy, 1993] we limit ourselves to Korzhinsky's very succinct conclusion for the simplest cases of periveinous and contact metasomatism. This conclusion was made like the conclusion of the equation of infiltration zoning.

Adopting as constant the diffusion coefficients of the components we get k equations of the form:

$$\frac{\partial i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} \quad (3.46)$$

In local chemical equilibrium the number of degrees of the free system is limited to the k equations of the thermodynamic link of the component's concentration and content.

Then in determined limited conditions, when the initial rock's composition is constant ($a = a^0 \dots, k = k^0$ for $x = 0, t > 0$) and the solution's composition is defined ($C_a = C_a^0 \dots, C_k = C_k^0$ for $x = 0$ and $t > 0$), the state of the zone of diffusion interaction depends upon only two parameters, x and t .

Observing the section that keeps constant the composition of component i , we get:

$$di = \left(\frac{\partial i}{\partial t} \right)_x dt + \left(\frac{\partial i}{\partial x} \right)_t dx = 0 \quad (3.47)$$

and substituting $\frac{\partial i}{\partial t}$ from (3.46) we get k equations of the form

$$\left(\frac{dx}{dt} \right)_i = -D_i \frac{\partial^2 C_i}{\partial x^2} \div \frac{\partial i}{\partial x} \quad (3.48)$$

For constant limited conditions and zones of constant composition the system of k equations in the form (3.48), through substitution of a variable $\frac{x}{\sqrt{t}} = W$, where $W = u^{dif}$, the section's adduced transfer speed, may be transformed into an equation of simple diffusion zoning:

$$\left(\frac{dx}{dt} \right)_{a \dots k} = -D_a \frac{\partial^2 C_a}{\partial x^2} \div \frac{\partial a}{\partial x} = \dots = D_i \frac{\partial^2 C_i}{\partial x^2} \div \frac{\partial i}{\partial x} = -D_k \frac{\partial^2 C_k}{\partial x^2} \div \frac{\partial k}{\partial x} \quad (3.49)$$

an equation legitimate for all the introduced limitations and the constant composition of the zones.

General properties of metasomatic diffusion zoning

Analysis of the diffusion equations and diffusion zoning allows us to reveal the main particularities and properties of diffusion metasomatism, of which we propound the results, referring the reader for detailed substantiation to the works of [Korzhinsky, 1969, 1982; Demin *et al.*, 1969; Guy, 1993; Zharikov, 1965; Balashov, 1992]. First of all we underscore the chief difference between diffusion and infiltration metasomatic zoning. While in the columns of infiltration metasomatism the components' concentration in the metasomatic zones remains constant, in the zones of diffusion metasomatism the components' concentration in the solution changes continually.

Analysis of the diffusion equation shows the following:

a) For the zones of removal of components $\frac{\partial C_i}{\partial t} < 0$ and $\frac{\partial^2 C_i}{\partial x^2} < 0$ (3.50).

Accordingly, the curves $C_i = f(t)$ for $x = \text{const}$ and $C_i = f(x)$ for $t = \text{const}$ are convex.

b) For zones of components' addition, on the contrary, $\frac{\partial C_i}{\partial t} > 0$ and $\frac{\partial^2 C_i}{\partial x^2} > 0$ (3.51)

and the curves $C_i = f(t)$, $C_i = f(x)$ are concave (for x and t constant, in conformity^{*}).

c) Curves $C_i = f(t)$ and $C_i = f(x)$ are suddenly nonlinear for feeble values of x and t and clearly strive to linear dependence as far as t and x grow. In other words for t and x very great, $\frac{\partial^2 C_i}{\partial x^2} > 0$ and $\frac{\partial C_i}{\partial x} \rightarrow \text{cte}$, and the diffusion equation may be approximately in linear dependence of the concentration gradient upon the distance.

d) It is established that, $\frac{\partial^2 C_i}{\partial t^2} < 0$, i.e. the variation speed of the component's concentration, in other words, the diffusion speed decreases in time. Similarly the absolute value $\left| \frac{\partial^2 C_i}{\partial x^2} \right| < 0$. and the variation speed of the concentration (diffusion speed) decreases with distance. For low t , the exact dependence

$$x = W\sqrt{t} \quad (3.52)$$

* Note that in the complex cases of configuration of reacting environments, the relations $\partial C_i / \partial t$ for various x may be more complicated. For instance, in the case of component i 's diffusion from the body's limit in infinite space for feeble X , C_0 at first increases then decreases, whereas for higher X we always have $\partial C_i / \partial t > 0$ (X is the body's distance from contact in an infinite environment).

where W is the adduced; diffusion speed, (one often takes approximately $x=\sqrt{2Dt}$). This correlation is well confirmed by experimental reproduction of the metasomatic diffusion columns. On fig.3.4 can be seen a few relations $x=f(t)$ for the diffusion columns of acid lixiviation and bimetasomatic reciprocal action [Zharikov & Zharisky, 1973; Zharikov, 1985; Zharisky, 1989]. It can easily be seen that speed W of growth of the limits of zones varies in wide intervals from 0.4 to 18 cm/year^{1/2} depending on the situation of the column's limit, the porosity, the composition and pH of the solution.

e) If there occurs in the diffusion zone a reaction of the solution with the solid rock, it is only possible with replacement of one mineral by another, i.e. it leads to appearance of a diffusion metasomatic zoning. In this case, equation (3.49) has a final solution:

$$(3.53) \quad \left(\frac{dx}{dt}\right) = -D_a \frac{\Delta\left(\frac{\partial C_a}{\partial x}\right)}{\Delta a} = \dots = -D_k \frac{\Delta\left(\frac{\partial C_k}{\partial x}\right)}{\Delta k}$$

in which the members have a real significance for the components taking part in the replacement reactions. On graph C - x , lines $\frac{\partial C}{\partial x}$ on these replacement limits undergo a fracture (positive or negative, depending on whether there is an addition or a removal of the given component). On fig.3.5 can be seen diagrams C - x and I - x for the simplest case of replacement of unicomponent mineral A by unicomponent mineral F with perifractural metasomatism, when initial concentrations at the source (fracture) and in semi-infinite space (surrounding rocks with one side of the fracture) are constant, C_f , C_a and C_f^0 , C_a^0 , respectively. A case is presented in which t is sufficient for concentration gradients to be linear. It is easily seen that at the limit where A is replaced by F : $A + (f) \rightarrow F + (a)$ (which usually manifests itself as $\rightarrow F | A \rightarrow$) $\Delta\left(\frac{\partial C_a}{\partial x}\right) < 0$, but $\Delta\left(\frac{\partial C_a}{\partial x}\right) > 0$, i.e. the concentration gradient of the reacting components is changing, which is graphically expressed by discontinuity of curve $\frac{\partial C}{\partial x}$. On fig.3.6 is represented the general case of replacement by one component mineral F of the bimineral rock $A+B$ (also composed of one component minerals). Conditions at the limits are similar only in the considered example: C_f , C_a , C_b is constant for $x=0$ and $x=\infty$, and thereby C_f is great compared with C_a and C_b for $x=0$ and, on the contrary, $C_a > C_b$, much greater than C_f for $x = \infty$. Time t is sufficient for the linear dependence in the concentration gradients. Owing to the difference of the components' concentration gradients and diffusion coefficients in the zone of reciprocal action on the initial rock $A+B$, there develops a column of metasomatic zones $\rightarrow F \Big| F+A \Big| A+B \rightarrow$. For component f , at each limit (II/I and

I/0), $\Delta\left(\frac{\partial C_f}{\partial x}\right) < 0$, which corresponds to an addition of component f and replacement of B by F (limit I/0) and A by F (limit II/I). Accordingly, curve $\frac{\partial C}{\partial x}$ has two concave discontinuities. Mineral B at limit I/0 is replaced by mineral F and component b is eliminated. Accordingly, for component b , $\Delta\left(\frac{\partial \varphi}{\partial x}\right) > 0$ and the line of the concentration gradient undergoes a convex discontinuity. For component a , equation (3.50) at limit I/0 has no solution because at that limit gradient $\frac{\partial C_a}{\partial x}$ does not change and, consequently, does not produce elimination or admission of component a . At limit II/I, $\Delta\left(\frac{\partial C_f}{\partial x}\right) > 0$ and mineral A is replaced by mineral F with removal of component a , addition of component f and, accordingly, the curves of the concentration gradient are sharply concave (for component a), and convex (for component f). Especially interesting is zone I, in which can change the content of components f and a and consequently that of minerals F and A . Without losing ourselves in discussing this complex situation, we may note that this problem possesses, evidently, only partial alternative solutions, the essence of which is reduced to the following. If molar density of minerals F and A is different, then, for maintaining the linear dependence of the components' concentration gradients at the limits of zone I, a variation is possible of the quantitative correlations of the minerals (cf. fig.3.6). On the contrary, for proximate molar densities the composition of the zones will remain constant, since the components' dissolution or precipitation could lead to breaking the linear dependence of their concentration gradient.

- f) The main difference of diffusion metasomatic columns consists in the behavior of the minerals, the solid solutions at the limits of metasomatic zones. Since gradient of concentration of components at the zone limits continuously varies, correspondingly the diffusion components' content also varies in the minerals of variable composition. The composition variation of the minerals, solid solutions at the zone limits, is a characteristic sign of diffusion metasomatic zoning (differing from infiltration).
- g) The columns of metasomatic diffusion, as well as those of infiltration arise under the influence of the components' differential mobility and are therefore characterized by reduction of the number of minerals in the zones as far as intensity of the initial rocks' metasomatic transformation increases. Apart from this fundamental zoning, for diffusion metasomatic columns, a complementary zoning is usually observed, which sometimes predominates and is formed by reaction minerals for whose appearance conditions are favorable in which there is uninterrupted, continuous variation of concentration of the added and

removed components. Complementary zoning, as we have mentioned, is distinguished by an equal number of minerals in contiguous zones.

Bimetasomatic zoning

Bimetasomatic zoning is of special interest amidst diffusion metasomatic formations, arising during slow penetration of solutions in the contact zone between two environments in chemical unbalance. Owing to the difference of concentrations (more exactly of chemical potentials) of the components, there is observed in contact regions diffusion of components, accompanied by formation in the diffusion zone of a few metasomatic zones composed of reaction minerals (if of course formation is possible of minerals composed of diffusing components).

For clarity's sake we consider two more simple cases of bimetasomatic reciprocal action between one component minerals A and B , forming reaction minerals composed of components a and b . On figure 3.7 are given diagrams of concentration/distance ($C-x$) and of content/distance ($i-x$) in the cases when components a and b produce reaction minerals of constant composition. The diagram is established for a kind of time $t > t_0$ when as a result of reciprocal reaction action of components a and b a bimetasomatic column is formed in the zone of oncoming diffusion:



As far as reaction minerals have a constant composition, the content of components in the zones constantly and jerkily varies from zone to zone. The components' concentration gradients continually vary, and at the zone limits, curve $C_{a,b} = f(x)$ presents a discontinuity in answer to the final solution $\Delta\left(\frac{\partial C}{\partial x}\right)$, positive in case of a component's removal (convex fracture) and negative in case of addition (concave fracture). In course of time the zones increase without change of the column's structure. Growth speed diminishes according to equation (3.52) $\left(W = \frac{x}{\sqrt{t}}\right)$.

On figure 3.8 can be seen the column's structure and diagrams of concentration ($C_{a,b}$)/distance (x) and contents of components (a,b)/distance(x) in case of bimetasomatic reciprocal action of minerals with one component A and B , with formation of reaction zones composed of minerals of variable composition corresponding to the content of components a and b . Comparing the column of figures 3.7 and 3.8 it can easily be seen that in the last case, at the limits of zones composed of mineral-solid solution, a variation in their composition takes place:

0.0 4 3 2 1 0
 $\leftarrow A \mid \text{from } A_9B_1 \text{ to } A_8B_2 \mid \text{from } A_7B_3 \text{ to } A_6B_4 \mid \mid \text{from } A_4B_6 \text{ to } A_3B_7 \mid \text{from } A_2B_8 \text{ to } A_1B_9 \mid B \rightarrow$

And then, adopting a limited miscibility of components a and b (in the limits indicated above) in relation to which a zoning is formed, with ultimate change of composition and the gradient of the components' concentration at the zone limits. If AB were characterized by complete miscibility of the components, there might arise, between A and B removals, a unique zone of the mineral AB : $\leftarrow A \mid AB \mid B \rightarrow$. The column introduced above (cf. fig. 3.8) grows without structure change, with slowing down in time according to equation (3.52).

The considered examples of bimetasomatic zoning are obviously of the most simple. In more complicated cases, for example with some diffusing components and minerals with several components, of content either constant or variable, the column's structure is more complex and one may vary in time according to the value of diffusion coefficients of the components and their concentration gradients (gradients of activity) in the reacting environments and the influence of the varying solution upon the composition's activity. These situations demand each time their concrete solutions.

However, even in the simplest cases the essential changes in the structure of the columns are established for contact conditions not plane, but curved contact of the reacting environments. Without devilling on a theoretical analysis of these cases [Korzhinsky, 1969, 1982; Zharikov & Vlassova, 1961] we examine by way of concrete illustration the influence of contact forms upon the structure of bimetasomatic columns.

On figure 3.9 for zoning with reaction minerals of constant composition (cf. fig. 3.7), is shown the correlation of thickness of different zones for a convex (I) and a concave (II) contact (relative to environment A). The diagram is constructed with calculation of the balance of components a and b , necessary for the formation of reaction zones in the same relations as in the case of plane contact considered above (cf. fig 3.7).

It can be easily seen that in the environment limited by a curved contact there arises a progressive growth of the zones, linked to the fact that the volume of replacing rocks decreases in course of time. This is very neatly expressed for the most external limit ($\rightarrow A_3B \mid A \rightarrow$ on fig. 3.9, I $\rightarrow AB_3 \mid B \rightarrow$ on fig. 3.9, II). After a certain time t the initial rocks A or B may be totally replaced, conditions at the limits being essentially different, as well as the speed and even the direction of displacement of the limits (limit $A_2B \mid AB_2$). On the side of the convex contact the limits' displacement speed will slow down not only corresponding to $x=W\sqrt{t}$ but also on the strength of the volume increase of replaced rock (contact surface always grows, especially for the most external

front). Finally for a certain time t progress of the external zone may stop, and the following zone will progressively replace the external one.

In general conclusion, when contacts are incurved, sharp asymmetric bimetasomatic columns appear. This is particularly important in case of bimetasomatic columns of skarns linked with selective replacement of determined zones by superposed mineralization.

3.5. Complex types of metasomatic zoning

The equations and properties of infiltration and diffusion metasomatic columns examined above obviously represent extreme types of metasomatic zoning. But it is impossible not to note that even these extreme approximations will suffice to unravel the structure peculiarities of many natural metasomatic formations. Besides, in the general case, natural metasomatic processes are complex phenomena, whose dependence upon main parameters has been expressed above in generalised equations of matter flows (3.13) to (3.20). Meanwhile a complete open solution of the general flow equation is for a present lacking. Partial solutions have been obtained and researched for the process combinations most widely spread in nature for associated processes of infiltration and diffusion [Zharikov, 1965, Zharikov & Vlassova, 1961; Balashov, 1985; Guy, 1993], for diffusion processes complicated by kinetic reaction [Balashov & Lebedeva, 1989; Balashov & Lebedeva, 1991], for infiltration in space with temperature gradient [Korzhinsky, 1953, 1969]. Without going into details of these complex theoretical models we give a succinct account of the results.

Metasomatic zoning of infiltration – diffusion

Infiltration metasomatism accompanied with diffusion is usual in natural metasomatic processes. In reality, to such a type (with a more or less great role of diffusion) belong most natural metasomatic columns. Only, in order to determine the respective role of infiltration and diffusion in such or other columns, a painstaking and labour-intensive study must be made of mineral-solid solutions at all the zone limits, in so far as constancy (for infiltration) or variableness (for diffusion) of their content are the only general and indubitable criteria of difference. Such detailed researches are often inaccessible, therefore are isolated examples of well studied complex columns of infiltration-diffusion [Zharikov, 1968; Zharikov & Vlassova, 1961; Vlassova & Zharikov, 1975].

Let us briefly examine the structure peculiarities of infiltration–diffusion columns. The summary flow of component "i" $\left(I_i^S = \left(\frac{dm_i}{dt} \right)^S \right)$ is composed of

infiltration flow $\left(I_i^{\text{inf}} = \left(\frac{dm_i}{dt}\right)^{\text{inf}}\right)$ and diffusion flow $\left(I_i^{\text{dif}} = \left(\frac{dm_i}{dt}\right)^{\text{dif}}\right)$ that can be composed provided the acting forces are expressed according to the equation of growth speed of entropy (3.19). Then

$$I_i^S = I_i^{\text{inf}} + I_i^{\text{dif}} = L_i^{\text{inf}} X_i^{\text{inf}} + L_i^{\text{dif}} X_i^{\text{dif}} = L_i^{\text{inf}} \frac{\nabla p}{T} - L_i^{\text{dif}} \frac{\nabla \mu_i}{T} \quad (3.54)$$

In isothermal conditions in a one-dimension space:

$$\left(\frac{dm_i}{dt}\right)^S = \left(\frac{dm_i}{dt}\right)^{\text{inf}} + \left(\frac{dm_i}{dt}\right)^{\text{dif}} = L_i^{\text{inf}} \frac{\partial p}{\partial x} - \frac{L_i^{\text{dif}} RT}{C_i} \cdot \frac{\partial C_i}{\partial x} \quad (3.55)$$

Replacing kinetic coefficients by the usual filtration and diffusion coefficient and putting the expression of the acting forces, as was done above for a unitary section ($q=1$) we get:

$$\left(\frac{dm_i}{dt}\right)^S = \varphi_i C_i \omega_i - D_i \frac{\partial C_i}{\partial x} = \omega_i C_i - D_i \frac{\partial C_i}{\partial x} \quad (3.56)$$

where, remember, $\varphi_i = \frac{\omega_i}{\omega_0}$ is the coefficient of filtration effect and ω_0, ω_i are the speeds of filtration of the flow and component "i" ($\omega_0 = \omega_i$ for $\varphi_i = 1$).

Consequently, following the same path as at the conclusion of the equation of infiltration zoning (cf. above but also [Korzhinsky, 1951a, 1969, 1982; Zharikov & Vlassova, 1961]) we further make the following transformation. Taking from (3.56) the derivative on distance x and replacing $\frac{\partial}{\partial x} \left(\frac{dm_i}{dt}\right)^S$ by $\left(-\frac{\partial i}{\partial t}\right)^S$ where i is the component i 's content in the unitary volume, we get:

$$-\left(\frac{\partial i}{\partial t}\right)^S = \omega_i \frac{\partial C_i}{\partial x} - D_i \frac{\partial^2 C_i}{\partial x^2} \quad (3.57)$$

Choosing a section where component i 's content is constant (i.e. $di = 0$), for which:

$$di = \left(\frac{\partial i}{\partial t}\right) dt + \left(\frac{\partial i}{\partial x}\right) dx = 0 \quad (3.58)$$

in sum we get:

$$\left(\frac{dx}{dt}\right)_i^S = \omega_i \frac{\partial C_i}{\partial x} \div \frac{\partial i}{\partial x} - D_i \frac{\partial^2 C_i}{\partial x^2} \div \frac{\partial i}{\partial x} \quad (3.59)$$

an equation expressing the relative transfer speed of the determined section (with constant composition of component i), as a result of the common infiltration and diffusion transfer of the component.

Equation (3.59) may obviously take the form:

$$\left(\frac{dx}{dt}\right)_i^s = \left(\frac{dx}{dt}\right)_i^{inf} + \left(\frac{dx}{dt}\right)_i^{dif}$$

(3.60) or:

$$u_i^s = u_i^{inf} + u_i^{dif}$$

(3.61)

where $u_i^s = \left(\frac{dx}{dt}\right)_i^s$ is the general speed of the flow, equal to the section's transfer speed owing to infiltration:

$$u_i^{inf} = \left(\frac{dx}{dt}\right)_i^{inf} = \omega_i^{inf} \frac{\partial C_i}{\partial x} \div \frac{\partial i}{\partial x}$$

(3.62)

and of the transfer speed of the section of matter diffusion:

$$u_i^{dif} = \left(\frac{dx}{dt}\right)_i^{dif} = -D_i \frac{\partial^2 C_i}{\partial x^2} \div \frac{\partial i}{\partial x}$$

(3.63)

Equation (3.39) may also be expressed in dependence upon volume of infiltrated solution since $dv = \omega_0 dt$, and evidently:

$$\left(\frac{dx}{dv}\right)_i^s = \varphi_i \frac{\partial C_i}{\partial x} \div \frac{\partial i}{\partial x} - \alpha D_i \frac{\partial^2 C_i}{\partial x^2} \div \frac{\partial i}{\partial x}$$

(3.64)

For an “established” state of the process, i.e. if we adopt the limits examined above, constancy of all coefficients and of conditions at the limits, and constancy of concentrations gradient and others, then, in the system of k equations of type (3.59) or (3.64), dependence between x and t or x and v is established and the equations may be replaced by one adduced variable. Then equation:

$$\left(\frac{dx}{dt}\right)_i^s = \left(\frac{dx}{dt}\right)_a = \left(\frac{dx}{dt}\right)_b = \dots = \left(\frac{dx}{dt}\right)_k$$

(3.65)

or

$$\left(\frac{dx}{dv}\right)_i^s = \left(\frac{dx}{dv}\right)_a = \left(\frac{dx}{dv}\right)_0 = \dots = \left(\frac{dx}{dv}\right)_k$$

(3.66)

will describe the zone limits in a complex column of infiltration-diffusion. Equations (3.65) or (3.66) have a final solution for components taking part in a replacement reaction of minerals with one another at the zone limits.

Let us consider in a most simple example the properties of diffusion-infiltration zoning. Suppose, as a result of the solution's infiltration, through complicated diffusion of components, there will arise transfer of a one component mineral A by another one component mineral F with formation of a complementary zone of complex reaction mineral AF , that has a variable composition. On fig.3.10 is represented as resulting from it the column $\rightarrow F | AF | A \rightarrow$, for which are constructed diagrams of concentration, (C_a, C_f) , distance (x) , and components' content in the zones (a, f) distance (x) . It is easily seen that each zone newly formed $(F | AF)$ consists of two parts, a front one of diffusion and a rear one of infiltration. At the limits of the diffusion parts there are gradients of concentration of the diffused components and, at the limits of the infiltration parts, the components' concentration remains constant. Components' content at the limits of the diffusion part of the zone, composed of a mineral of variable composition, change and so does the composition of the mineral-solid solution from A_3F (this is the composition adopted as limit for the replacement of the initial mineral x) up to AF_2 (this composition is adopted for the zone's infiltration part). At the limits of the diffusion part of zones F , its composition remains constant, since F is a mineral of constant composition, in the limits of the infiltration parts of the zone, their composition is constant, as is that of the mineral - solid solution.

The relative thickness of the parts of diffusion and infiltration of the zones depends upon the respective transfer speeds of the corresponding limits. It is natural for the column's diffusion part to exist if $u^{dif} > u^{inf}$. In the contrary case ($u^{inf} > u^{dif}$) it does not take place. These correlations are clearly illustrated in graph $x - t$ (fig. 3.11). The transfer speed of the infiltration limit is constant and the transfer distance is $x^{inf} = u^{inf} t$, or $x^{inf} = w_0 t$ if the reaction speed of the diffusion at the limit is great (w_0 is the speed of the solution filtration). The speed of transfer of the diffusion limit is inversely proportional to $t^{1/2}$ and $x^{dif} = u^{dif} \cdot t^{1/2} \cong (2Dt)^{1/2}$. It easily seen that $x^{inf} = x^{dif}$ for $t = \frac{2D}{(w_0)^2}$. The relations

$\frac{x^{dif}}{x^{inf}} \rightarrow 0$ or $\frac{(2D)^{1/2}}{w_0 \cdot t^{1/2}} \rightarrow 0$ i.e. if $2D$ is much smaller then $w_0^2 \cdot t$, the diffusion part of the zones will be entirely pressed by infiltration flows.

Attempts have been made to evaluate the real relations of speeds limiting the diffusion and infiltration processes [Zharikov & Zaraysky, 1973; Vlassova & Zharikov, 1975; Zaraisky, 1989; Flecher & Hoffman, 1974; Guy, 1993]. From experimental data and informatic and analogical modelling it can be with fair certainly deduced that diffusion speeds for high temperatures

amount to $n \cdot 10^{-6} - n \cdot 10^{-4} \text{ cm}^2/\text{sec}$, which determines transfer speeds of diffusion limits in microporous rocks in order of $n \cdot 10^{-6} - n \cdot 10^{-4} \text{ cm}^2/\text{sec}$ or $1.8-18 \text{ cm/year}^{1/2}$. Consequently, filtration speed, being of a few decimetres a year, which corresponds to permeability of about $n \cdot 10^{-1}$ millidarcys, will practically crush the zoning's diffusion part and, on the contrary, for permeability lower than 10^{-3} millidarcys the column's structure will essentially be a diffusion structure.

Note an important property of the diffusion-infiltration columns (cf. fig. 3.10): columns arise by diffusion (for feeble t); in course of time the infiltration parts' capacity increases and, for greater t the columns form essentially through infiltration with complicated diffusion fronts of replacement.

Metasomatic zoning in conditions of temperature gradients

A temperature variation during a metasomatic process brings about in definite conditions essential variations in the structure of metasomatic columns. The equation of joint transfer for that case may be written:

$$I^S = I^{\text{inf}} + I^{\text{dif}} + I^{\nabla T}$$

(3.67)

or

$$\left(\frac{dm_i}{dt}\right)^S = \left(\frac{dm_i}{dt}\right)^{\text{inf}} + \left(\frac{dm_i}{dt}\right)^{\text{dif}} + \left(\frac{dm_i}{dt}\right)^{\nabla T} = L_i^{\text{inf}} \cdot \frac{\nabla p}{T} - L_i^{\text{dif}} \cdot \frac{\nabla \mu_i}{T} + L_i^{\nabla T} \cdot \frac{1}{\nabla T}$$

(3.68)

Meanwhile the latter's general solution is lacking. Let us examine a few partial real situations in natural procuresses. A first case concerns components' diffusion in a situation of thermal gradient. If there exists a temperature gradient in space, it exerts practically no influence upon the structure of diffusion metasomatic columns. Heat transfer in natural metasomatic systems (up to 700°C) takes place substantially more quickly than components' diffusion [Korzhinsky, 1969, 1972]. Coefficients of thermal conductivity are about $n \cdot 10^{-4} - n \cdot 10^{-3} \text{ cm}^2/\text{sec}$, whereas the components' diffusion coefficients, as noted above, vary from $n \cdot 10^{-7}$ to $n \cdot 10^{-5} \text{ cm}^2/\text{sec}$.

Abstractly such a case may of course occur when under whatever external influence a substantial temperature gradient is maintained a long time in the system. Then, due to the dependence of diffusion coefficients upon temperature, the linear approximation to the solution of the equation of diffusion is uncertain, and the structure of the diffusion column may vary in time. In this case also, however, the system will tend to a stationary state when the thermo-diffusion flow will be equilibrated by the usual one or, as it is called in these cases, the flow of chemical diffusion ($I^{\text{dif}} + I^{\nabla T} = 0$).

In conditions of temperature variation in time there occurs a variation of the diffusion coefficients and of the zones' growth speed. As far as the diffusion coefficients dependence upon temperature, the different components have the same sign, no structure variation of the columns must take place. However, an important temperature decrease produces of course regressive mineral reactions in the column.

Let us now consider the situations arising in infiltration metasomatism when there is a temperature gradient. In so far as the filtration speeds are compared with the speeds of heat transfer through conduction and surpass them, a real situation frequently occurs in nature when infiltration metasomatism develops in conditions of temperature gradient in space. Such various processes of contact elimination are most neatly exemplified from which arise greisenization and formation of secondary quartzites.

In case of infiltration metasomatism in conditions of spatial temperature gradient, component i 's general flow will fold up from its own infiltration flow and from the component's flow due to temperature gradient ($I^S = I^{inf} + I^{VT}$) or:

$$\left(\frac{dm}{dt}\right)^S = \left(\frac{dm}{dt}\right)^{inf} + \left(\frac{dm}{dt}\right)^{VT} \quad (3.69)$$

It can be shown that the concentration gradient of saturation in space, as function of temperature proves to be the component's acting transfer force in a field of thermal gradient. Then for the one dimensional flow of component " i " we shall have:

$$dm_i = \left(\varphi_i C_i - L_i \frac{\partial C_i}{\partial x} \right) w_0 dt \quad (3.70)$$

where φ_i is the coefficient of filtration effect, L_i the proportionality coefficient at the replacement of the acting forces (it corresponds to a quantity of the component transferred from the solution for a unitary gradient). Equation (3.70) can take the form:

$$\frac{dm_i}{dt} = \varphi_i w_0 C_i - L_i w_0 \frac{\partial C_i}{\partial x}, \quad (3.71)$$

which answers equation (3.69).

Omitting the conclusion that was made of the perfectly analogous conclusion of the equation of infiltration zoning, in sum we get the following equation of infiltration metasomatism in conditions of a field of thermal gradient:

$$\left(\frac{dx}{dv}\right)_i = \varphi_i \frac{\partial C_i}{\partial x} \div \frac{\partial i}{\partial x} - L_i \frac{\partial C_i^2}{\partial x^2} \div \frac{\partial i}{\partial x} \quad (3.72)$$

For k components we shall have a system of k equations of the form (3.72).

In order to analyze this system of equations it is necessary to have given (or determined from concrete conditions) limitations of condition and dependence.

D.S. Korzhinsky has thoroughly studied the case in which through the rock infiltrates a solution in equilibrium with it and, entering a contact zone with a temperature gradient, begins to react with the surrounding rock. Such cases correspond to conditions $I^{\text{inf}} = 0$, $I^S = I^{\nabla T}$ or in equation (3.71) and (3.72), $\left(\frac{dm}{dt}\right)^{\text{inf}} = 0$, then:

$$\left(\frac{dx}{dt}\right)_i = -L_i \frac{\partial^2 C_i}{\partial x^2} \div \frac{\partial i}{\partial x} \quad (3.73)$$

Since the components' saturation concentration depends upon temperature there will occur a quantitative variation in the mineral composition of the surrounding rocks, up to the appearance of metasomatic zoning, expressing the saturation concentration's (C^{sat}) dependence upon distance. As far as $C^{\text{sat}} = f(T)$ and $T = f(x)$ it is evident that $C^{\text{sat}} = f(x)$. The metasomatic column, arising in course of time, will grow with the variation of the quantitative correlation of the minerals that produce a structure change of the column. The latter will be expressed in the disappearance of some zones and the appearance of others.

As an example, fig.3.12 shows the somewhat changed diagram [Korzhinsky, 1982] indicating rise and development of a metasomatic zoning for a linear dependence of the saturation concentration (C^{sat}) upon temperature (which in turn is a linear function of the distance). The diagram on fig.3.12a shows this dependence for components a , b , d , f and g . On fig.3.12b the metasomatic zoning is schematically reproduced for columns composed of minerals with a single component A , B , D , F and G .

At the linear dependence of saturation concentration $C^{\text{sat}} = kx + k$, it is easily seen that $\frac{\partial C^{\text{sat}}}{\partial x} = k$ and $\frac{\partial^2 C^{\text{sat}}}{\partial x^2} = 0$. Then, in conformity with equations (3.71), (3.72) and (for the examined case) $\left(\frac{dm}{dt}\right)^{\text{inf}} = 0$, we shall have $\left(\frac{\partial i}{\partial v}\right) = -k$. This means that in proportion as the solution infiltrates for components having a positive k , their content and that of the associated minerals will decrease. In the examined case it is components b and d and minerals B and D . On the contrary, for k negative, when the components' saturation concentrations (in other words their solubility) decreases, content of components

decreases in proportion of percolation and there occurs precipitation of the corresponding minerals, components a , f and g (cf. fig. 3.12a). Moreover, for the last two it is admitted that saturation concentration is reached in proportion of the solution's infiltration at T_2 (for component f) and T_4 (for component g).

The schematic diagram on fig 3.12b clearly shows the structure change in time ($v = w_0 t$) and distance (x) of the metasomatites. Owing to percolation of solutions in virtue of the mentioned dependence of C^{sat} upon T and x in the initial mineral paragenesis $A+B+D$, there begin replacement reactions of minerals B and D , which will dissolve through precipitating mineral A (which is indicated by arrows: $\uparrow$ dissolution, $\downarrow$ precipitation). Except mineral A , at limit x_2 and temperature T_2 , saturation concentration of added mineral F will be reached and then, further in the dissolving column, minerals $B \uparrow + D \uparrow$ will be replaced by the precipitating minerals $F \downarrow$ and $A \downarrow$. At limit x_4 (isotherm T_4) saturation concentration of another added component g will be reached, and dissolving minerals B and D , will be replaced by three minerals A , F , and G . It is schematically shown how the metasomatic column will vary in proportion of the solutions' infiltration (i.e. in course of time) in whatever point x in the space chosen by us of unidimensional thermal gradient (cf. fig. 3.16). The diagram is clear enough.

A few explanations will suffice. To construct the diagram the usual conditions of metasomatism have been adopted, when there exist free volumes, and, as shown above, pressure on the solid phase exceeds that of the fluid. In these conditions the solution dries up, and the saturation concentration corresponds to such conditions $p^S > p^f$. To construct the diagram it has been admitted that for x from 0 to x_3 $C_a^{sat} > C_f^{sat}$, for x from x_3 to x_6 $C_f^{sat} > C_a^{sat}$, and for the whole range of x $C_a^{sat} > C_g^{sat}$. In consequence of these dependences, after v_4 in zone $x_4 - x_6$ there begins dissolution of earlier precipitated G , but in zone $x_2 - x_4$ precipitation of mineral F . The final structure of the column for high v (v_6) will be $\rightarrow A | F \rightarrow$, and all remaining minerals will be replaced by those that develop the greatest crystallization pressure in determined parts of the column.

Let us now consider, on an even more simple example, the general case when the rock is penetrated by a solution in unbalance with it and forming an infiltration zoning that develops in conditions of temperature gradient in space (equation 3.71 and 3.72, where $I^S = I^{inf} + I^{VT}$). Into the initial rock composed by one component minerals A and B , let a solution penetrate, oversaturated in a one component mineral F . For this, $p^F > p^A > p^B$. In the infiltration zone there is a temperature gradient defining a linear dependence of saturation concentration (when $p^S > p^{fl}$) upon distance. Then $k' = \frac{\partial C^{sat}}{\partial x}$ is positive for component b and its solubility increases with distance; for components f and a , k' is negative; moreover, with whatever x , C_a^{sat} becomes

higher C_f^{sat} . On fig.3.13 are represented diagrams $C^{sat}-x$ and $v-x$, on which is clearly seen that on a neat infiltration column $\rightarrow F | F + A || A + B$ (the double line separates the initial rock) are superposed quantitative changes, of content of precipitating (F, A) and dissolving (B) minerals, that finally produce a structure change of the columns.

The simplest cases have been examined above, but as far as the solubility's dependence upon temperature (and distance) may be complicated, the structure, correspondingly complicated and varying in time, will possess metasomatic columns.

We have underscored above that infiltration columns with temperature gradient are particularly characteristic of processes of elimination at contact. Let us consider as illustration a typical column of endocontact greisenization, where arrows accompanying the mineral symbols indicate quantitative changes in minerals' content taking place in the zones (c.f. fig.3.14, structure of a column, taking no account of accessory components). Note that if zones 1,2 and in some measure 3 have a coarse extension, then in the internal zones 4 and 5 the variations are localized as veins and periveinous changes, and their volumes are substantially smaller than those of the external zones (we conventionally translate this into a conical graph).

Variation of temperature in time influences saturation concentration, bringing about a concomitant variation in the growth speeds of the zones and in quantitative correlation of the minerals. Most remarkable is the fixation to retrograde replacements of the column's initial minerals.

Other complex types of metasomatic zoning

In connection with the dependences reported above (equations 3.20, 3.29 and others) other complex types of metasomatic zoning are theoretically possible and also occur in nature in determined conditions.

For instance, there is infiltration zoning, with variation (in space) of the coefficient of filtration effect (ϕ_i), for a substantially different value ϕ_i of the components, for example for the passage of a wave of acid components, infiltration and diffusion zoning in conditions of substantial value of replacement speed of the minerals and, more generally, of kinetic reactions. Also possible are other complex combined influences of the factors of equilibrium and dynamics of metasomatism upon content and peculiarities of structure of the metasomatites.

Infiltration zoning through passage of a wave of acid components was examined by D.S.Korzhinsky (1982). He showed that solubility and activity coefficients of the chief acid components depend upon the solution's general acidity. Consequently there occurs in the infiltration zone of the solutions a "mineral" differentiation: in the zone of action of the acid wave

“basic” minerals will be eliminated and replaced by “acid” minerals. The real forms of distribution of the minerals are defined by concrete dependences of components’ solubility and activity coefficients upon the “structure” of the wave of acid components.

Infiltration metasomatism has not been especially studied in environments with different coefficients of the filtration effect. However, utilizing researches on the filtration effect by Zharikov, 1969, Zharikov *et al.* 1973, one may propound two main cases. For an insignificant variation of φ_i the column structure remains unchanged; what does change (according to equation 3.34) is the transfer speed of the limits of the zones and the column as a whole. For substantial changes, and especially those in various directions of φ_i , the column structure will be different and, owing to the concentration’s dependence upon φ (c.f. equations 3.7, 3.10) it may vary in time with the appearance and disappearance of separate zones.

Metasomatic zoning complicated by kinetic phenomena was not studied by D.S.Korzhinsky, his theory of metasomatic zoning being founded on the principle of total local chemical equilibrium. However, in many natural metasomatic columns, a divergence is observed from the condition of equilibrium: in many cases they are insignificant and negligible, but in a few others they are essential. The problem of the role of kinetic parameters has been examined by [Zharikov, 1971; Golubev, 1970; Rusinov, 1972; Balashov, 1985; Balashov & Lebedeva, 1989; Zaraysky *et al.*, 1989; Lichtner, 1991].

The inventory on principle of the role of the kinetic factor follows from equations (3.14, 3.15, 3.20). In isothermal conditions

$$I_i^S = I_i^{\text{inf}} + I_i^{\text{dif}} + I_i^{\text{kin}} \quad (3.74)$$

or

$$\left(\frac{dm_i}{dt}\right)^S = \left(\frac{dm_i}{dt}\right)^{\text{inf}} + \left(\frac{dm_i}{dt}\right)^{\text{dif}} + \left(\frac{dm_i}{dt}\right)^{\text{kin}} \quad (3.75)$$

Substituting the expression of the acting forces for isothermal conditions we get:

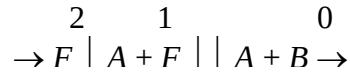
$$\left(\frac{dm_i}{dt}\right)^S = L_i^{\text{inf}} \cdot \nabla p - L_i^{\text{dif}} \cdot \nabla \mu_i^{\text{dif}} - L_i^{\text{kin}} \cdot \nabla \mu_i^{\text{kin}} \quad (3.76)$$

The second member of equation (3.76) may be replaced in more usual correlations by noting it, for example, through the chemical affinity (A_i) and fullness of flow of reaction ξ_i [Khaaze, 1967; Prigogine & Defay, 1963]:

$$\left(\frac{dm_i}{dt}\right)^{\text{kin}} = -L_i^{\text{kin}} \cdot \nabla \mu_i = A_i \frac{d\xi_i}{dt} \quad (3.77)$$

or we may obtain a more complex expression through speeds of chemical reactions. Combining $I^s = I^{in} f + I^{kin}$ or $I^s = I^{dif} + I^{kin}$, one can essentially characterize infiltration or diffusion metasomatism with kinetic phenomena. Examining these questions in more detail, with abundant mathematical computations (Balashov & Lebedeva, 1991) would go outside the frame of this book; so, in order to characterize the main peculiarities of this kind of columns, we shall consider a simple example (fig.3.15).

We have already examined the isothermal infiltration column, formed of unicomponent minerals



At the zone limits develop replacement reactions at a final (observed) speed comparable to the solution's filtration speed. At limit I mineral B is replaced by minerals F and A (with $C_f^{sat} > C_a^{sat}$); at limit II mineral A is replaced by mineral F ($F \rightarrow A$). We thus agree that the replacement reactions are of the first order, depending upon concentration (content) of the replaced component. So at limit I, where occur parallel reactions of replacement of B by F and A :

$$\frac{df}{dt} = k_f \cdot b$$

(3.78')

$$\frac{da}{dt} = k_f \cdot b$$

(3.78'')

$$\text{And } \frac{db}{dt} = -(k_f + k_a)b$$

(3.78''')

where a , b , f are contents of unicomponent minerals A , B , F ; let us moreover take $k_f > k_a$. At limit II where mineral A is replaced by mineral F ; correspondingly

$$\frac{da}{dt} = -k_a^2 \cdot a$$

(3.79')

$$\text{and } \frac{df}{dt} = k_a^2 \cdot a$$

(3.79'')

If the speed of replacement reaction is feeble (diverging from the condition of local equilibrium) instead of sharp replacement fronts there appear zones of gradual replacement, at limit I of zone 1^{kin} , where occurs the replacement $A + F \rightarrow B$, and at limit II of zone 2^{kin} with replacement $F \rightarrow A$. The breadth of the "kinetic" zones depends upon time, the sine qua non condition for total disappearance of the replaced mineral (respectively, B and A) and

consequently depends upon reaction speeds k_f , k_a , k_a^2 and the minerals A and B 's contents in the initial rock and the infiltration part of the zone. Quantitative correlations of minerals at the limits of the kinetic zones are determined by the solution of kinetic equations (3.78 and 3.39) in the limits set by the content of components (minerals) in the initial rock and by the number of infiltration zones, which arouses no particular difficulties (Baguner, 1959; Benson, 1964; Zharikov, 1971).

On fig. 3.15 is indicated the structure of the examined column, where the breadth of "kinetic" zone parts is adopted for complete clarity. In nature kinetic phenomena are only observed at low temperatures and in superficial conditions and, characteristically, usually "kinetic zones" do not exist, as in the abstract example of fig.3.15. The portions with mineral relicts not replaced to the end are preserved in the form of separate spots in portions of uneasily circulating solutions. We shall pursue in the following chapter examination of the kinetic factors of metasomatism.

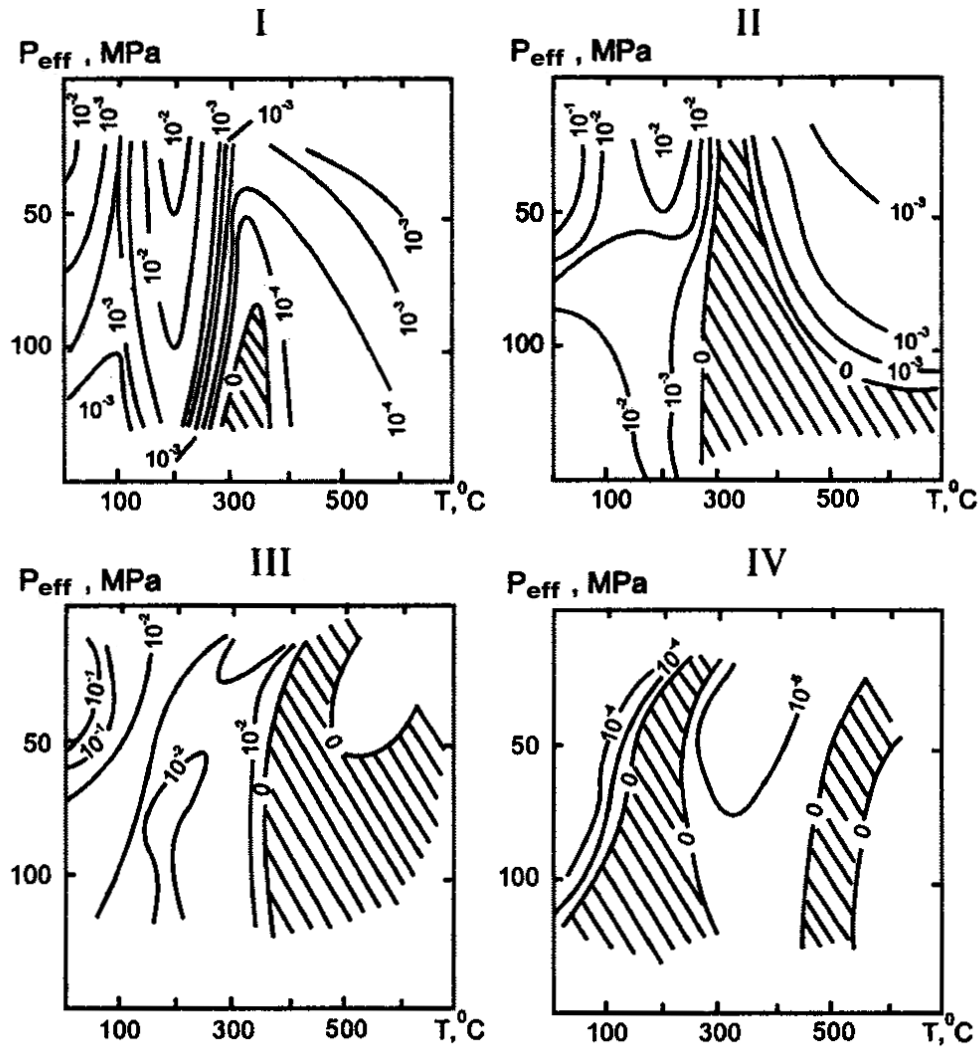


Fig. 3.1 Isopermeability depending on temperature and effective pressure for models of granodiorites (I), marbles (II) and garnet (III) and wollastonite (IV) skarns. Metric lines expressed in millidarcys ($1 \text{ mdarc} = 10^{-15} \text{ m}^2$). The hatched parts are “non-permeability” of rocks at given T-P. For these sections $k < 10^{-5}$ millidarcys.

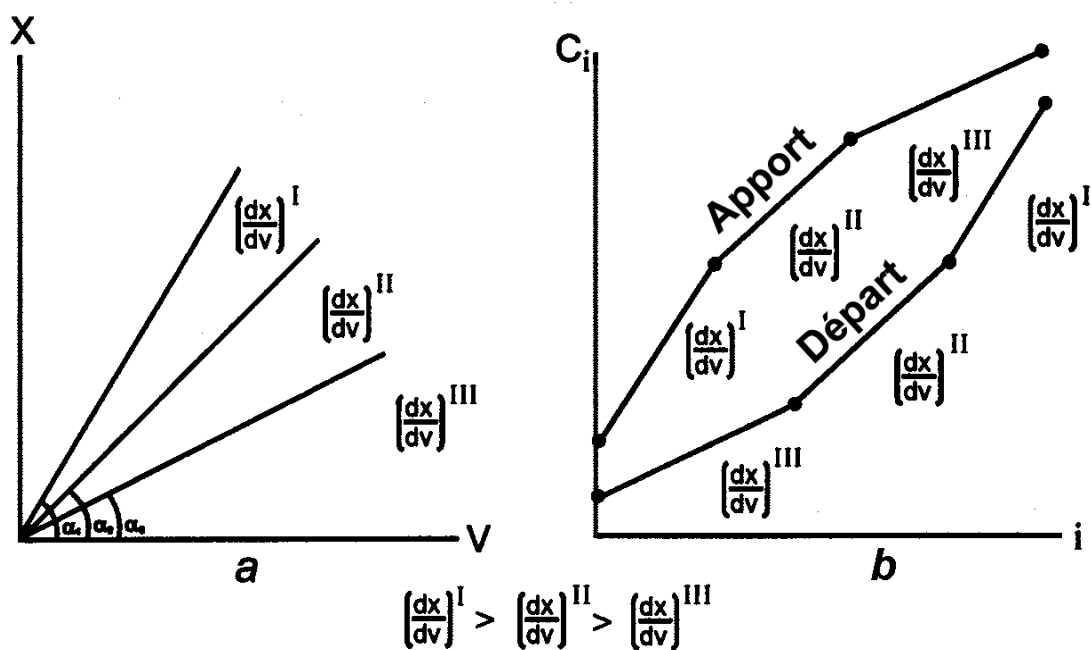


Fig. 3.2 Relative transfer speed of section $(dx/dv) = \tan \alpha$ (a) and relative variation of content (i) and concentration (C_i) of component i (b) within zones and at limits (replacement fronts) at chosen correlations $(dx/dv)^{I,II,III}$ in cases of addition and removal of components.

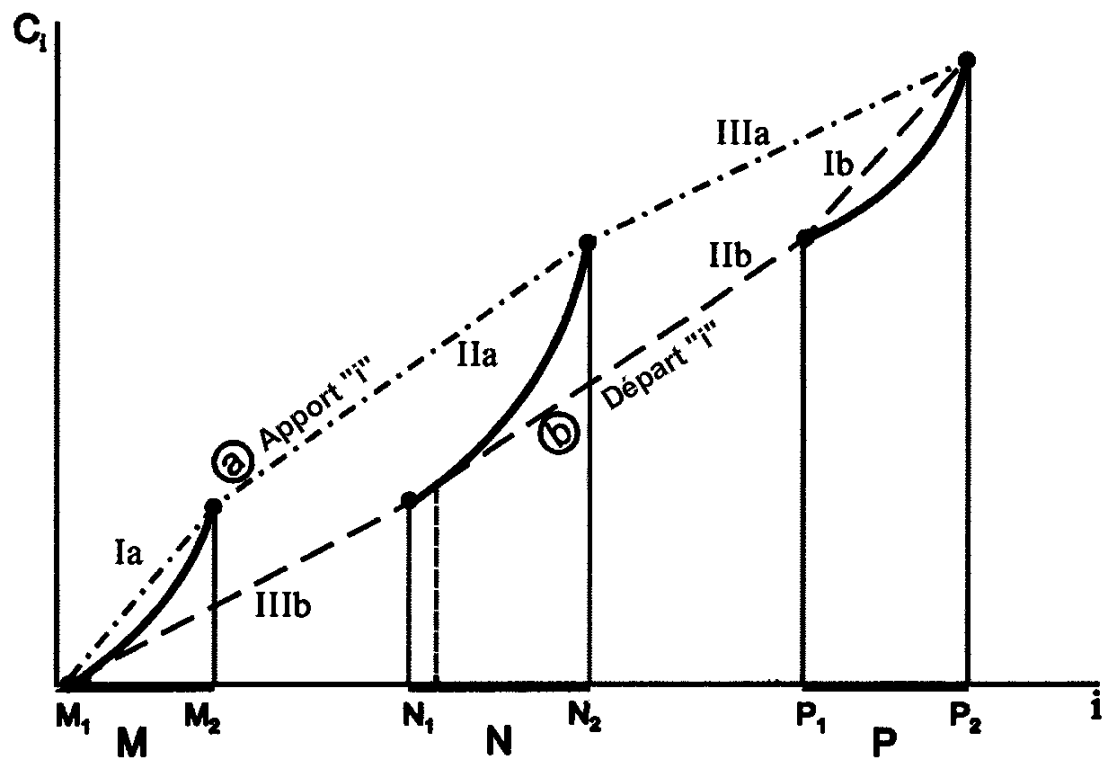


Fig. 3.3 Replacement reactions in columns with minerals of variable composition.

On the diagram are shown relations $C_i - i$ for minerals of variable composition M ($M_1 - M_2$), N ($N_1 - N_2$), P ($P_1 - P_2$) and relations x/v for fronts of addition (Ia, IIa, IIIa) and removal (Ib, IIb, IIIb) of component "i".

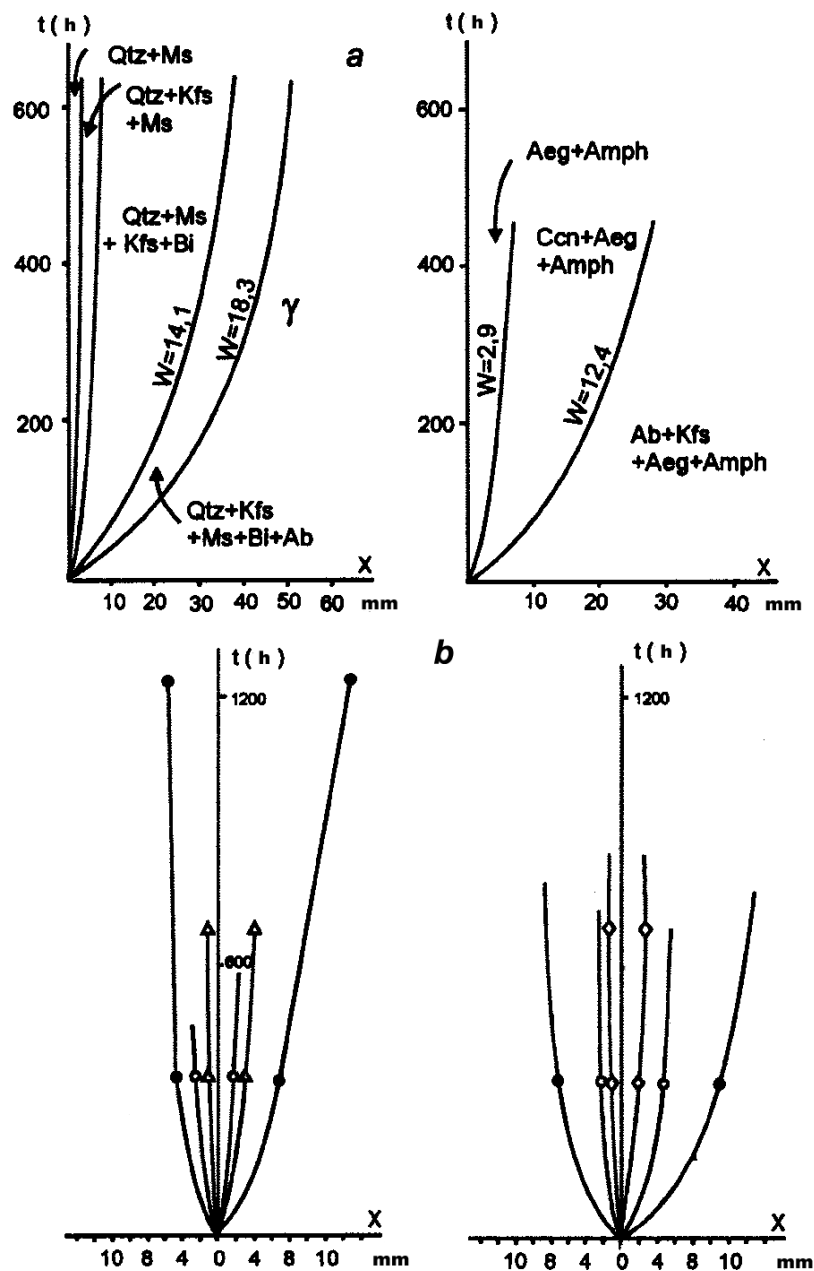


Fig.3.4. Growth speeds of periveinous diffusion (a) and bi-metasomatic columns (b). On the graphs $x=W\sqrt{t}$ designating mineral composition of corresponding zones and speeds ($W \text{ cm/year}^{1/2}$) of displacement of the external limits of the zones.

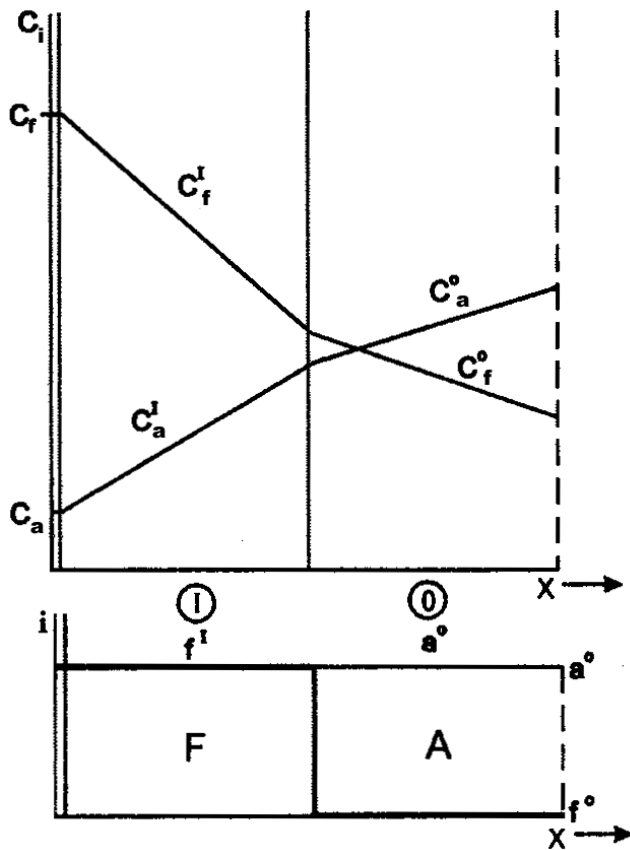


Fig. 3.5 Variation of concentrations (C_i) and contents (i) of components in zone of diffusion exchange of minerals of constant composition (mineral A replaced by mineral F).

Reciprocal diffusion action of fissure with semi-infinite space (only part of which is shown, by limited points) with stable concentration C_f and C_a for considerable t , when dC/dx approaches linear dependence.

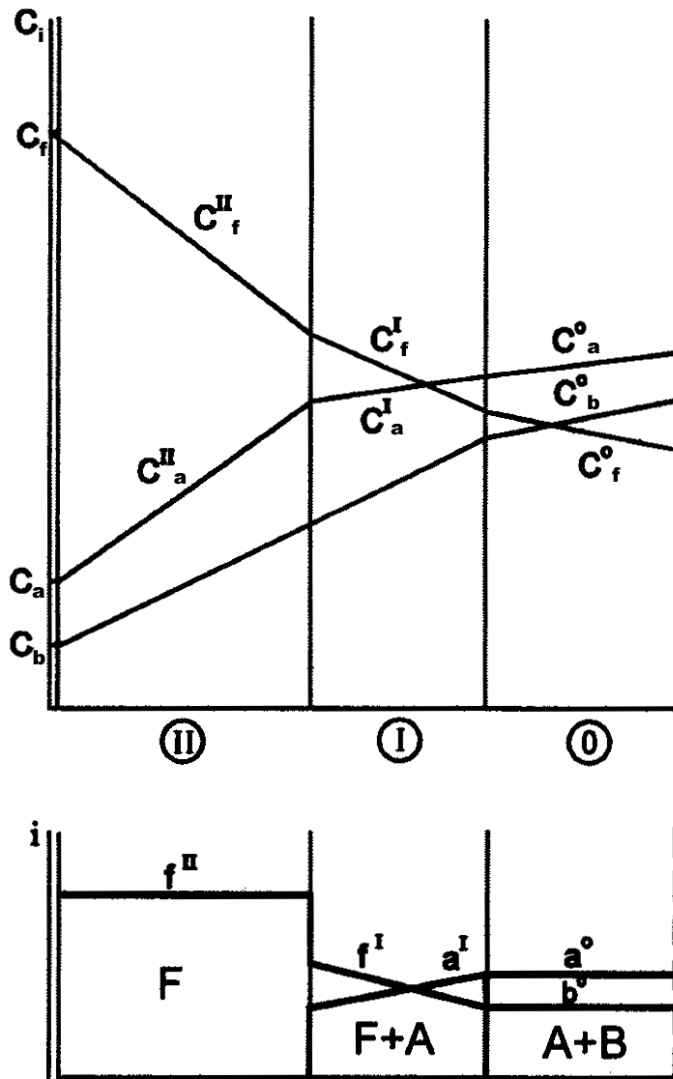


Fig.3.6 Variation of concentrations (C_i) and contents (i) of components in zones of diffusion replacement of minerals of constant composition.

Initial rock A+B is replaced by mineral F with formation zonality $F \text{ } F+A \mid A+B \rightarrow$. Reciprocal diffusion action of the source (fissure) with the semi-infinite space with constant initial concentrations C_f , C_a , C_b and C_f^0 , C_a^0 , C_b^0 for time t , when dC/dx approaches linear dependence.

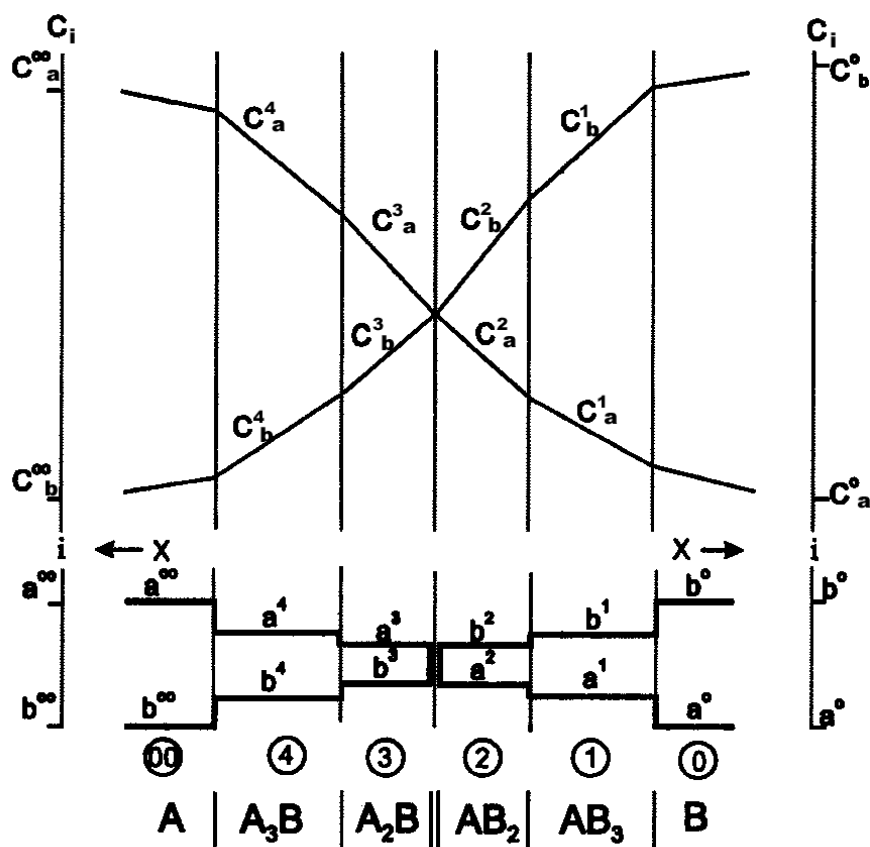


Fig.3.7 Diagrams of concentration of components (C_a , C_b) - distance (x) and content of components (a, b) - distance (x) at a determined moment $t \gg t^0$ for a bimetasomatic column with reacting minerals of constant composition.

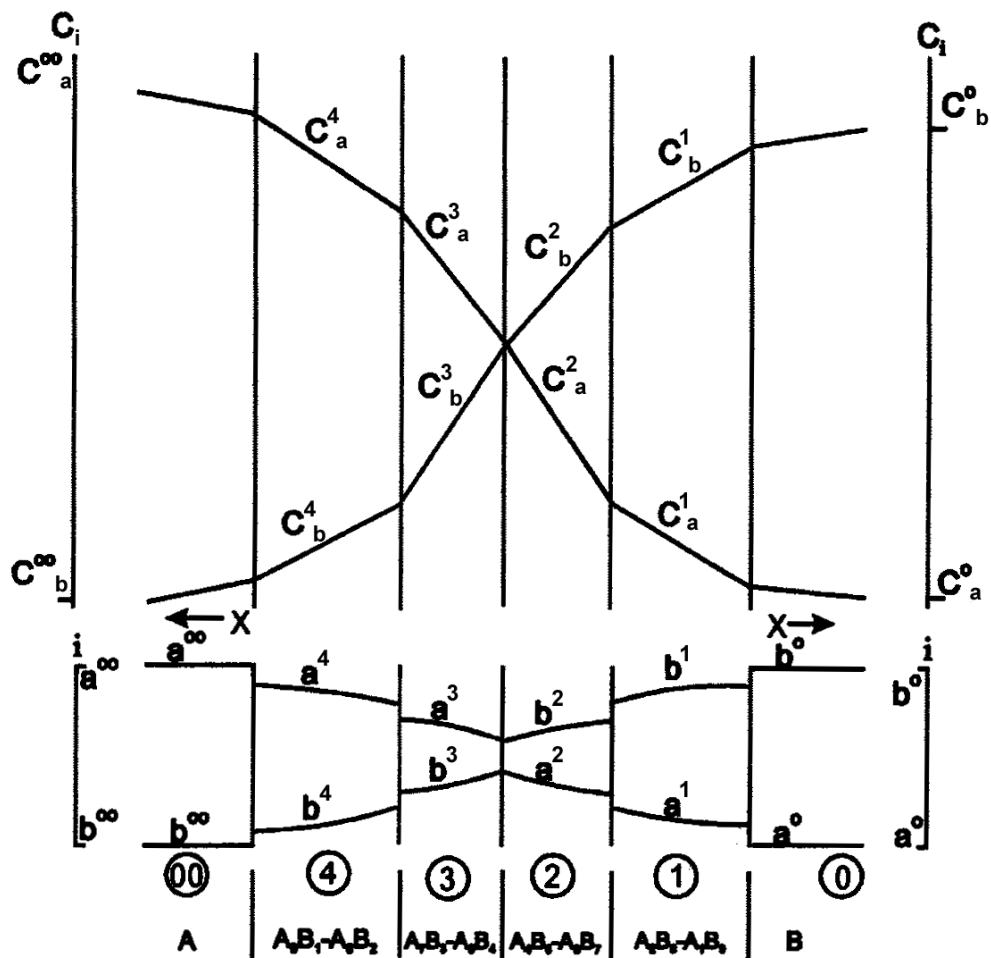


Fig.3.8 Diagrams of concentration of components (C_a , C_b) - distance (x) and content of components (a, b) - distance (x) at a determined moment $t \gg t^o$ for a bimetasomatic column with reacting minerals with variable composition.

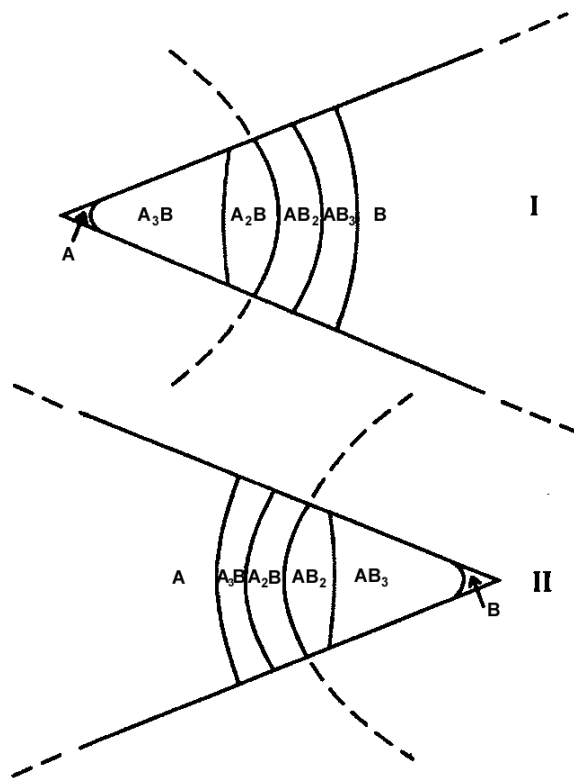


Fig.3.9 Correlation of thickness of bimetasomatic zones at curved contact surfaces.

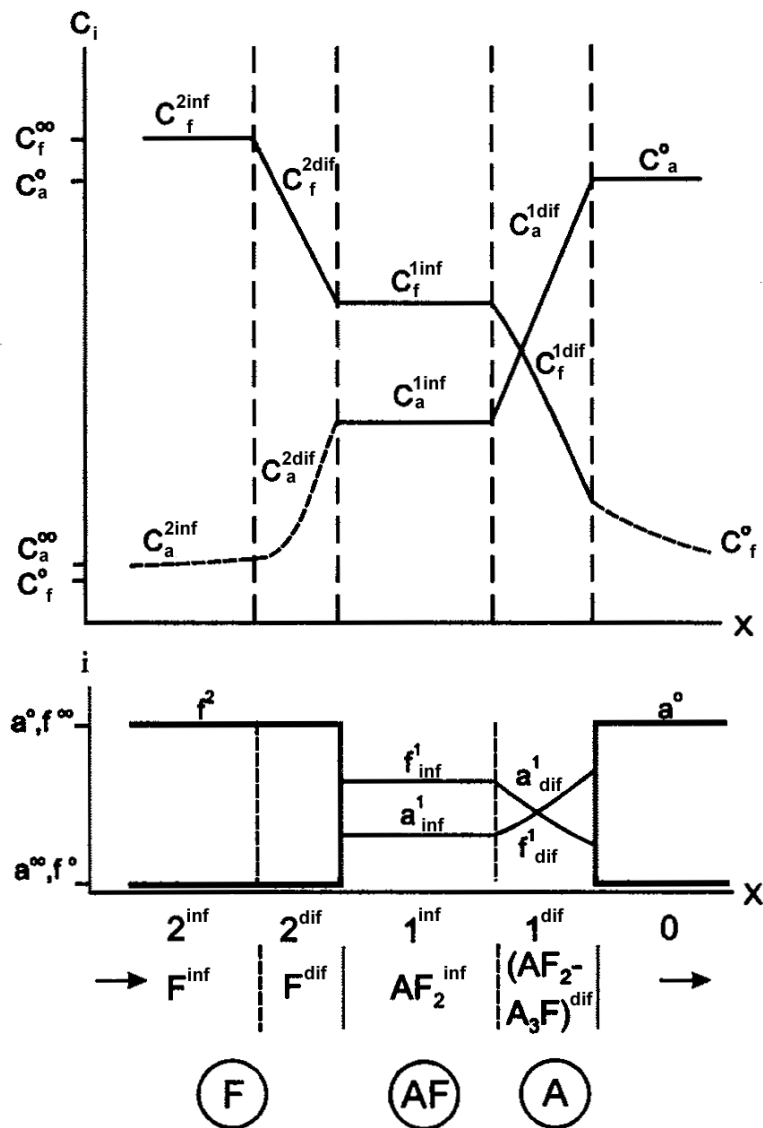


Fig.3.10 Diagrams of concentration of components (C_a , C_b) - distance (x) and content (a, b) - distance (x) for diffusion-infiltration column for any time $t > t^0$. Minerals A, F of constant composition, mineral AF of variable content.

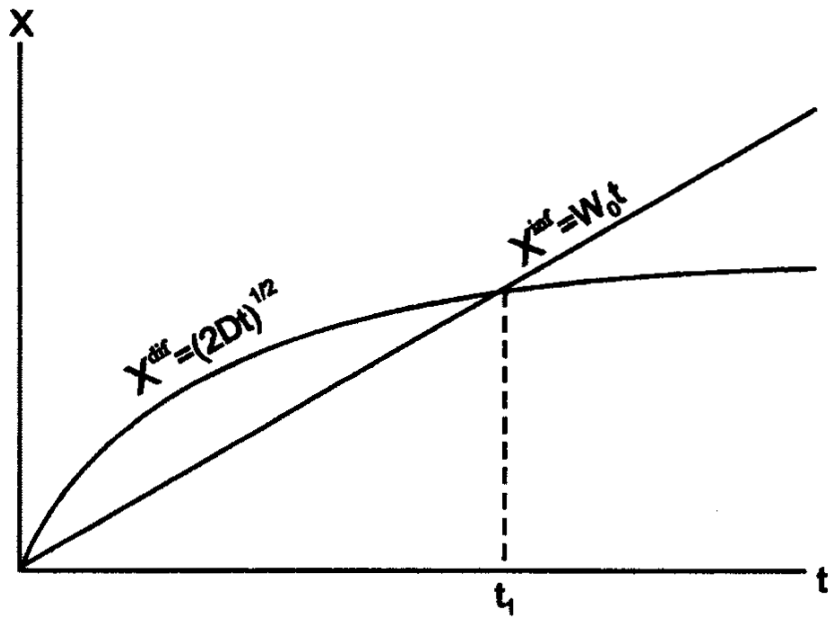


Fig.3.11 Diagram of distance (x) - time (t) for infiltration ($x^{\text{inf}} = w_0 t$) and diffusion ($x^{\text{dif}} = (2Dt)^{1/2}$).

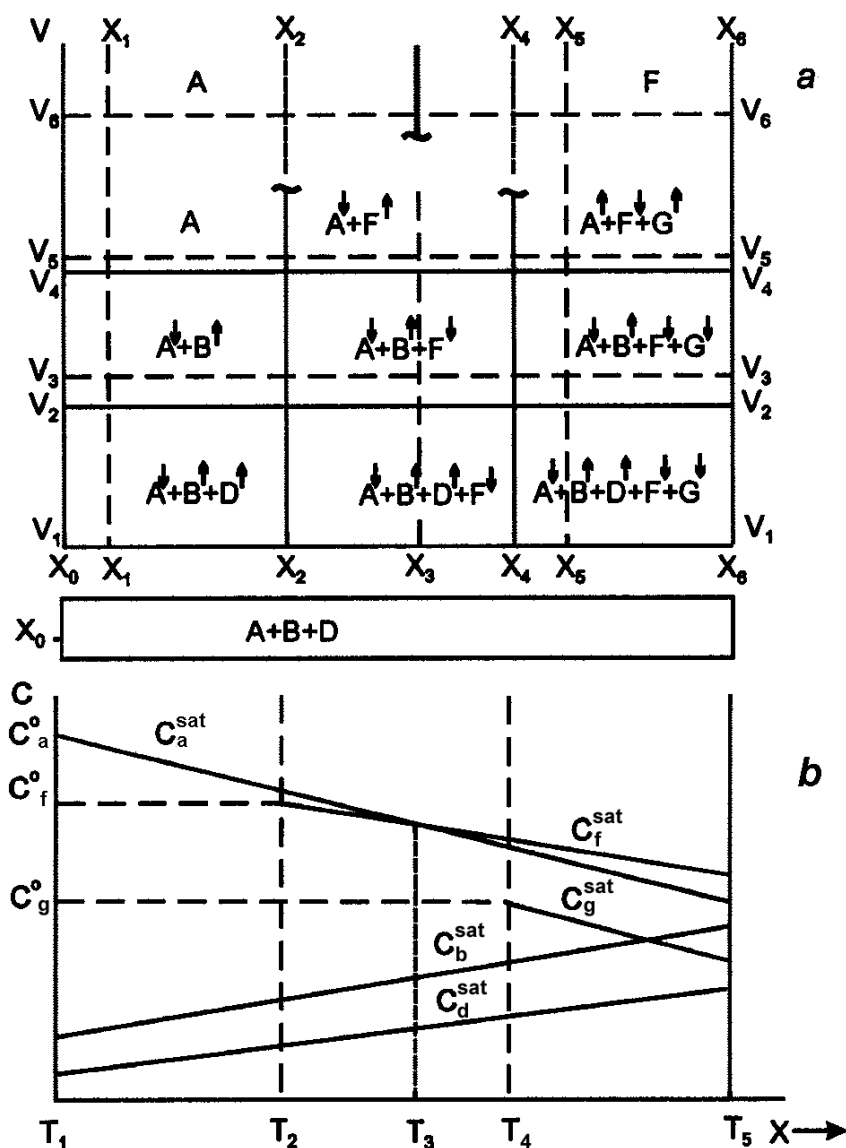


Fig. 3.12 Structure of metasomatic infiltration columns, arising in conditions of temperature gradient during continuous infiltration of solutions in equilibrium with the rock.

C^0 is initial concentration; C^{sat} is concentration of saturation; A,B,F are unicomponent minerals, upward arrows are dissolution and removal; downward arrows, addition and precipitation; v is volume of percolating solutions; x is distance; $v_1 - v_2$ is the structure of column at determined time ($v = w^0 t$); $x_1 - x_2$ are variation of composition of rock in given section as far as the solution percolates, i.e. with time.

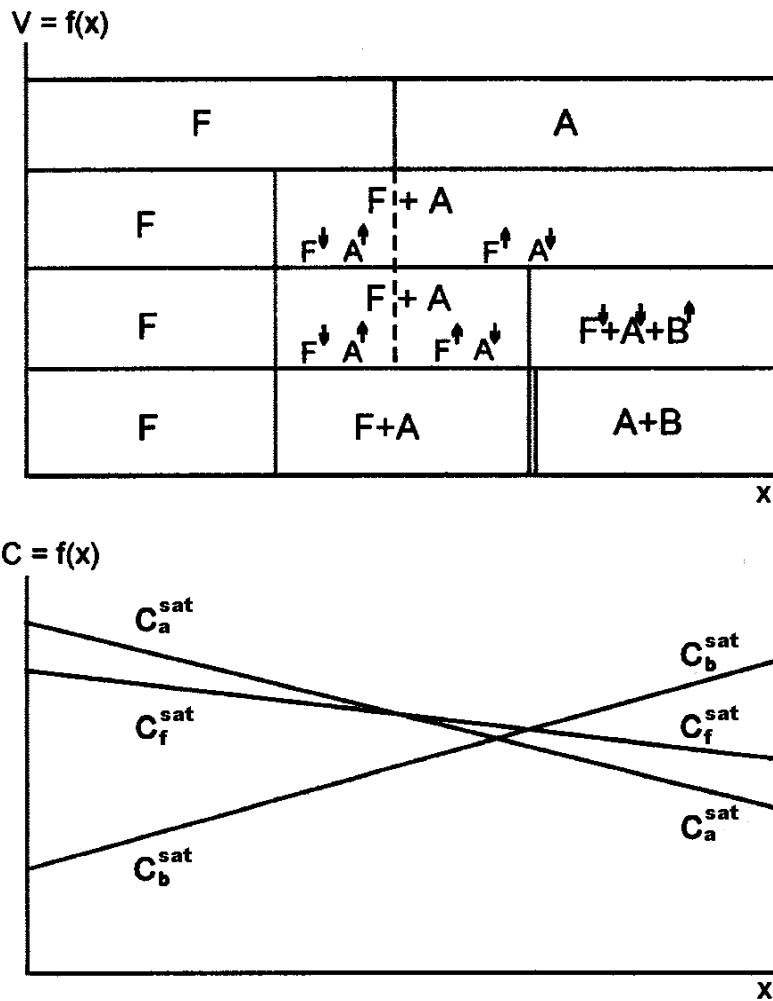


Fig.3.13 Structure variation of metasomatic infiltration column as far as solution percolates (v) owing to dependence of concentration of saturation upon distance (x) to the axis of the column.

Conventional signs, cf. Fig.3.12.

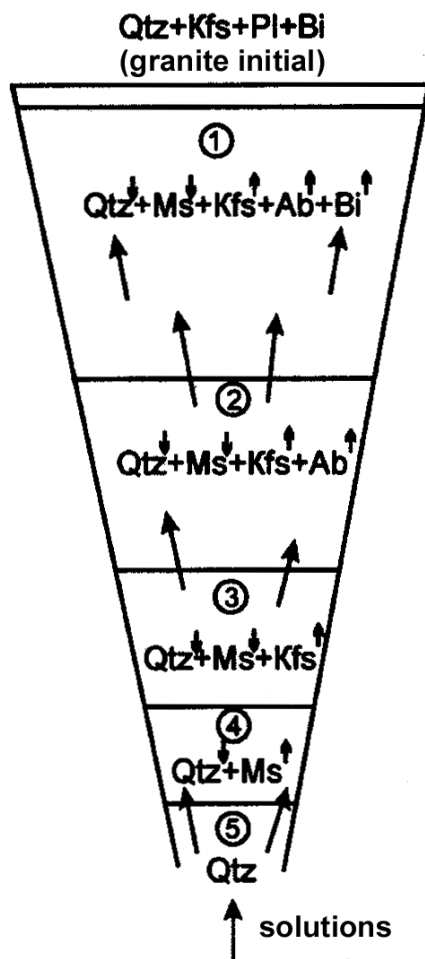


Fig.3.14 Schematic structure of usual greisens column.

Upward arrows, dissolution of minerals; downward arrows, precipitation of minerals.

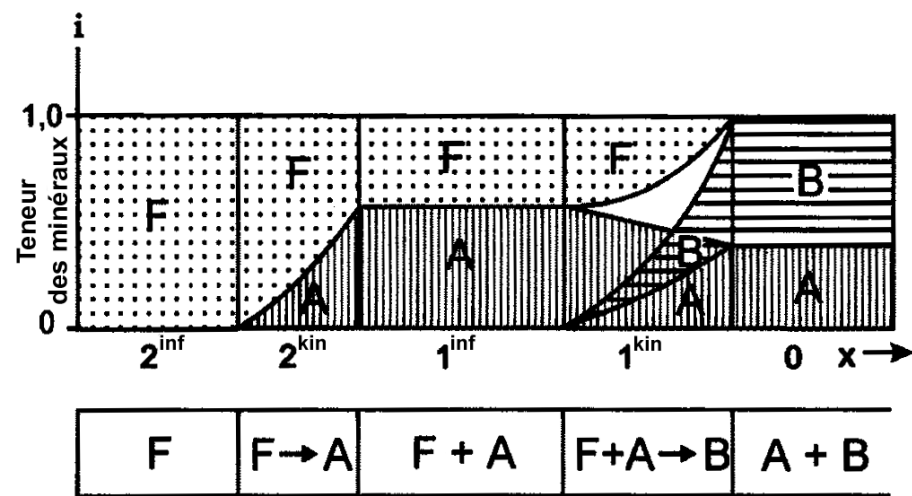


Fig.3.15 Infiltration column with kinetical transitions between zones.

Chapter 4

Kinetics of reactions and self-organization of metasomatic systems.

4.1. Mechanisms of metasomatic reactions

The mechanism of evolution of metasomatic reactions is defined by a series of conditions, the most important of which is the aggregate state of the substances taking part in the reactions of matters. According to this principle are distinguished gaseous, solid and properly hydrothermal metasomatism. The first two, although implying replacement of a mineral by another, are not all of them typical manifestations of natural metasomatism.

Gaseous metasomatism is manifested, for instance, on contemporary volcanoes, where they are observed on the walls of smoke-holes. Temperature of the gas-jets reaches 300-400°C and under the atmospheric pressure liquid water is absent in the jets. However, a reaction crust of neo formations in the hole-wall is a few millimeter thick. Moreover, while the gases diffuse into the rock, the walls of reciprocal action of theses gases with the rock rapidly decrease their temperature and condense the water. Therefore nearly at once a liquid aqueous solution is assisted by saturation of the surrounding rocks by superficial waters. It can even provoke a further transformation of the rock. In rare cases can purely gaseous metasomatism be observed. Hydrogen sulfide being chased by vaporization through a burning ferruginous splinter, the latter can be replaced by iron sulfides, but the geological significance of such a process is negligible. That gaseous metasomatism occurs on a small scale is accounted for by the feeble reciprocal action of the gases with the surface of minerals, their sorption being minimal. Therefore the superficial energy of the mineral grains constituting the rock does not perceptibly diminish in the reciprocal action with the gas and is a high energetic barrier on the way of gas-rock chemical reactions. Within the rock the gas can only penetrate the porous system, but its diffusion at the intergranular limits is impeded by the fact that the gas does not moisten the grains' surface and there is thus no capillary effect. All that strongly diminishes

dissolution of the minerals in the gas, and there appears only a substitution through diffusion within the solid phase, a very slow process, limited in space.

Replacement reactions of minerals in the solid phase are also of limited significance. They are polymorphous transformation conversions, isomorphous substitutions and decomposition of solid solutions.

Polymorphous conversions are in themselves pseudomorphous replacements of an initial mineral by a newly formed one, without change in the chemical content, but with variation of the symmetry of the crystalline net. Conversion of high temperature β quartz to α quartz at lowering of temperature to less than 573°C may serve as an example. The external shape of β quartz crystals is preserved, but the system changes from rhombohedral to trigonal. Experimental data about the transformation of α quartz into β quartz show that the process occurs at a mobile limit within the crystal that completely preserves its solid crystalline state. Before the replacement front there develop a series of thin twin-lamellas as preparatory stage to a complete transition to another polymorphous modification. On the strength of that, conversion occurs through a regrouping of atoms in the crystalline net in solid state; such reactions are energetically active and require a strong cooling down. That is why many polymorphous modifications of silica appear as a metastable formation far beyond the limits of their fields of stability. For instance trydimite and cristobalite appear as products of habitual low temperature neoformations in concretions of opal and silica, etc. on solfataric fields in actively volcanic regions.

Transformation conversions arise with change in the crystalline structure of the initial mineral or with variation of its content. This term was introduced to wide usage by V.A. Frank & Kamenetsky [1978] concerning phyllosilicates and the gradual change of a foliated silicate into another, neglecting the dissolution stage, but preserving the main or characteristic structure motive of the crystalline net. The mechanism is based on diffusion in solid phase inside the grain. An example of transformation can be seen in the initial stage of the biotite's vermiculitization, a formation of hydrated biotite. V.A. Frank & Kamenetsky and collaborators think there occurs, through this mechanism, a replacement of the minerals of the kaolinite group by hydromica and muscovite, and of smectite by muscovite [Frank – Kamenetsky *et al.*, 1978]. In experiments made by them at 500-700°C and 1Kb from kaolinite (unfoliated structure, triclinic system, modification 1Tk) they have obtained only the unfoliated sheet 1M. The bifoliated sheet of modification 2M can only be obtained, according to the authors, from bifoliated modification of minerals of the kaolinite group, i.e. from dickite. Correspondingly, trioctahedral mica (biotite) or chlorite may only be obtained from trioctahedral smectite and not from the dioctahedral one. According to these data, such conversion must be based on a succession of blocks or on the basis

of the crystalline structure of the initial mineral, without its dissolution. Endorsement of such wide distribution of the transformation mechanism in nature is discussed. Kinetic experiments [Zotov & Mukhamet Galeev, 1987] for low parameters (T up to 200°C , $P=P_{\text{sat}}$ of water) have shown the main evolution of an alternative conversion mechanism of kaolinite to mica through complete dissolution of the initial kaolinite. The transformation mechanism may be considered rigorously proved only for a process of feeble hydration of the phyllosilicates, for instance for the formation of hydrobiotite on biotite.

Isomorphous replacement is a process widely spread in nature, in which, by means of exchanges with the solution, the mineral's content changes with regard to parts of its components, with preservation of its structure frame at the solid state. Supposedly, isomorphous replacements occur with the help of diffusion at the solid stage. However, J. Wyart and Sabatier [Wyart and Sabatier, 1956] have shown that the phenomena of rearrangement and general diffusion of atom in the net of plagioclase takes place in the presence of water. Hydroxylated ions penetrate from the solution into the structure of the mineral, occupying the voids. In those places of the net there arise constraints, and the interatomic linkages weaken, forming channels in which the atoms move. Diffusion at the solid stage may play the main role in many isomorphous replacements. Experiments show this, for example, in the opposite diffusion of magnesium and iron through the granular limit of garnet and cordierite brought into contact [Guerassimov, 1992]. In the bordering regions of crystals of both minerals there appear diffusion zones, 8 to 15 μm broad, with gradual change in the iron and magnesium content. A zone's breadth depends upon the diffusion speed and the duration of the process. This dependence served as basis for the development of a method to determine the speed of metamorphic reactions and the duration of processes of metamorphism. If in the example treated the diffusion exchange of components took place between phases, in another case, in skarns with wollastonite – hedenbergite the late parts of the solutions, with great manganese activity, penetrating to the grains' limits of these minerals have provoked manganese diffusion in both sides of the contact [Rusinov & al, 1994]. The diffusion zones were 5 to 20 microns broad. So, isomorphous replacement occupies only outside parts of the crystals and it is unlikely that they have a geological scale.

Disintegration of solid solutions with formation of pseudomorphosis of two, more rarely several, minerals newly formed from an initial mineral - solid solution is the most characteristic instance of diffusion in solid phase. This process's originality consists in the fact that it can occur either as quasi-static (in quasi-equilibrium) or in manifest unbalance (spinodal decomposition). In the former case, there suddenly form germs (exsolutions) of the final stable phase, which then grow without change of content. In the case of spinodal decomposition, appear at first embryos of phases within unsharp limits and are

hardly distinguishable in content from the matrix. Gradually, inasmuch as decomposition develops, the dimensions of the excretions grow and their composition changes, moving away from the matrix and nearing the content of the stable ultimate member of the isomorphous series. So does the process gradually composition through an uninterrupted series of metastable states with periodical undulatory distribution of concentration of components in the crystal, which testifies to appearance of self-organization in the system of solid solution products of decomposition.

Proper hydrothermal metasomatism is a capital geologically significant variety of metasomatism. Hydrothermal metasomatic reactions, occurring with the necessary participation of a liquid aqueous solution, the role of which has been often underscored by D.S. Korzhinsky, includes precipitation and dissolution of minerals. In this reaction as well as in another, two phases at least take part, a solid and a liquid one. In metasomatic reactions representing the sum of dissolution and precipitation reactions, at least three phases take part: two solid and one liquid. The liquid phase (as a rule an aqueous solution) is undersaturated compared to one of the solid phases and oversaturated compared to the other. That is why the first phase is dissolved and the second one precipitates instead. Dissolution of the mineral – reagent takes place at the moving limit of reagent – solution. The streak of solution between this limit and the surface of the precipitated mineral – product is usually about a few half score Å to a few half score µm thick, so that product precipitation occurs immediately after the reagent's dissolution, and at macroscopic scale, dissolution and precipitation appear as simultaneous processes. This replacement mechanism has been clearly enough demonstrated for instance in the sanidine's hydrothermal replacement by montmorillonite [Samotoin *et al.*, 1996]. Electronic microscope study of rhyolite submitted to hydrothermal montmorillonitization with the remarkable method of vacuum-metallization with gold has shown that replacement begins with dissolution of the sanidine crystals. On photographs of the sanidine surface it can be seen (fig.4.1) that in the initial stage holes are formed on the surface and then, from them channels and cavities, breaking the crystal into blocks. Form and orientation of the holes and channels depend upon the crystallographic indices of the grain's surface. The blocks have the distinct form of sanidine crystals and a fine graded relief of surface, testifying to a pseudo-ribboned mechanism of dissolution. Dissolution has taken place slowly in a feebly saturated solution; block construction can be seen on photos in natural light (fig.4.1,v). At the same time with dissolution there occurred precipitation of montmorillonite on the sanidine surface. Montmorillonite is formed in different parts in the whole volume of sanidine, where the dissolution voids have formed. Montmorillonite particles are oriented along the sanidine's crystallographic directions. The montmorillonite sheets

separate into fine details of relief and of the form of the surface of the blocks of dissolution of sanidine.

In some places, dissolution of initial minerals may forestall precipitation, and then are formed pores and granular cavities into which the minerals may be deposited through a mechanism of growth in a free space. Then there may be formed pseudomorphoses of minerals with no common component with the dissolved crystal. For instance in the lavas of the solfatara fields of volcanoes are usually present sulfur pseudomorphoses in phenocrystals of pyroxenes and feldspars (“impregnation”, according to V.M.Goldschmidt). In regions of active volcanism, at the rocks’ hydrothermal modification, partial pseudomorphoses of adular or albite in phenocrystals of magmatic plagioclase are equally typical. Secondary adular (or albite) replaces a marginal zone of the phenocrystal, but the central part remains empty (case of pseudomorphoses). In many epithermal deposits, the internal zones of the column of metalliferous metasomatites are intensively silicified with formation of lixiviation voids which fill up with quartz in the form of druse, or look as vein filling. In all instances cited above metasomatic reaction includes two heterogeneous reactions (dissolution and precipitation) and homogeneous ones in the solution, and it takes place with unfailing participation of a liquid, essentially aqueous phase. Water, with its molecules of bipolar structure, has a high dissolution capacity. Through reciprocal action with the crystal’s surface, it strongly diminishes the minerals’ dissolution energy, weakening the atomic linkages, at the grain’s surface, with the rest of the crystalline net.

Reciprocal reactions of dissolution and precipitation are a specific feature of metasomatism. The degree of this dependence determines in particular that of the succession of structural elements and of composition in the replacement processes. Near the composition or structure of reagent and product occurs replacement through the epitaxial mechanism and arise homoaxial pseudomorphoses. In some cases, dissolution of the crystal, for example of potassic feldspar, locally augments the porous solution’s alkalinity in the forming cavity and precipitation of minerals, even in the absence of elements in common with the initial crystal. So, in the rhyolites’ perimetalliferous metasomatism in epithermal polymetallic argentiferous deposits, carbonate, galenite and chlorite precipitate in places where orthoclase and plagioclase phenocrystals dissolve. Pseudomorphoses occur in which filling up takes place long after dissolution, and the products display no link with the initial mineral. Such are the pseudomorphoses of sulfur in the phenocrysts of pyroxene and plagioclase in rocks on active volcan, in silica on vegetal remnants (for instance silicified trees) and other pseudomorphoses.

Consequently the mechanism of hydrothermal metasomatic reactions depends upon the physico-chemical conditions of the process and the relation

between reaction speeds of dissolution and precipitation, i.e., upon those reactions' chemical kinetics.

4.2 Kinetics of metasomatic reactions

One of the main differences between metasomatic and metamorphic processes is the degree of equilibrium realization between rock and solution and the influence of kinetic reaction of mineral formation upon the nature of the mineral association forming there. Metamorphic processes are usually of long duration, thus comparable to the geotectonic events (rising of mantellic plume, riftogenesis, orogenesis, etc.) and are accompanied by relatively slow variations of the metamorphism's external parameters. Moreover, time fundamentally succeeds in establishing equilibrium between solution and rock. That is why researchers on metamorphic rocks deal principally with equilibrated associations of minerals. The problem of kinetic reaction of mineral formation arises only in some cases, during low temperature metamorphism, at formation of zonal grains of minerals due to slowness of diffusion inside the crystals, but also at appearance of coronarian and other structures, testifying to an incomplete local recovery of balance of the rock-solution system during variations of the metamorphism's parameters. In most cases, the long duration of the metamorphic processes and the slow variation of temperature and pressure allow the rock to attain equilibrium with the metamorphic fluids.

Metasomatic processes are usually of less duration and are caused by the solutions' flows and, consequently, happen in conditions of high concentration gradients, i.e. the processes are on the whole in strong unbalance. As shown by D.S.Korzhinsky, one can choose in the study of metasomatic formations domains to which one applies the principle of local or mosaic equilibrium. Such domains are the internal parts of metasomatic zones in a column of metasomatic zoning, where in each isolated point equilibrium is achieved between solution and rock, but the equilibrium parameters vary from point to point. However, the zone limits are characterized by an evident breach of equilibrium and replacement reactions of minerals of external zones by minerals of internal zones. It fairly often happens that amongst metasomatic rocks relicts are spread of prior associations or intermediate, metastable products of reaction of mineral formation. Diagnosis and analysis of these minerals' associations in unbalance require knowledge of kinetics of chemical reactions in general and metasomatic ones in particular.

The role of chemical kinetics is expressed by the general equation of the matter flow in metasomatism (cf. 3.13):

$$I^S = I^{\text{inf}} + I^{\text{dif}} + I \cdot \nabla T + I^{\text{kin}}$$

For a high speed of chemical reactions to the solution's diffusion and infiltration the last term of the equation may be neglected, but for a quick mass exchange and slow reaction in isothermal conditions, the kinetics' contribution to the total flow may become dominant and determine the nature of the minerals' formation.

Formal chemical kinetics is based on the theory of absolute reaction speed [Glesston & *al.*, 1948] describing fairly well the simple homogeneous reactions in the solution, the gas and other species of heterogeneous reactions. Metasomatic reactions are distinguished by their particular complexity, because they include as constituent parts at least 3 or 4 elementary reactions, of which not less than 2 are heterogeneous (dissolution of the initial mineral and precipitation of the new one).

Theory postulates that all reactions proceed through formation of an "active complex" absorbing "activation" by formation of energy and later dissolving into final products with energy secretion. Starting from these energetic representations, the theory gives the dependence of reaction speed upon the thermodynamic parameters of the active complex. Direct determination of the reactions' kinetic constants constitutes a very complex experimental problem, because they depend upon the reaction's path. The latter is very sensitive to the slightest nuances in the conditions of the experiment's realization and is therefore difficult to reproduce. Naturally the number of reactions of which we study the kinetics is limited, which compels to seek the possibility of evaluating the kinetic reactions with the help of thermodynamic values experimentally determined and calculated.

The dependence of kinetic parameters upon thermodynamic properties of initial and terminal stable products is not established from a general point of view. Research about this relation are part of the general problem of the link between dynamics and thermodynamics, a problem first raised by Boltzman in his N-theorem. It was the first step to applying the entropy notion to microsystems on the basis of kinetic equations, an idea further developed in its application to the microscopic scale in the works of I. Prigogine on thermodynamics of irreversible processes.

Kinetic and thermodynamic parameters of a system are linked to the equation of the second principle of thermodynamics. Combining the equation of the system's internal energy

$dU = TdS - PdV + \mu dm$ with the expression of the heat process we get

$dQ = dU + PdV - dW - Hd_m$, the balance of masses $dm = d_i m + d_e m$

and, considering that $U = H - TS$, R. Khaaze [Khaaze, 1967] brings the equation linking the thermodynamic variables and the kinetic parameters of the chemical reaction:

$$TdS = dQ + T S_{dn} + dW + A d\xi \quad (4.1)$$

Here is introduced the notion of chemical affinity of a reaction $A = \mu \cdot n$ (n is the stoichiometric coefficient in the reaction, μ is the component's chemical potential) and ξ is the (incomplete) transfer degree of the reaction ($0 < \xi < 1$), dW represents the dissipation of its own energy taking into account the work of the friction forces, the electric forces and others. Equation (4.1) shows that an entropy variation, being a function of the system's state, depends upon the energy exchange with the environment and upon the processes inside the system, including the kinetics of chemical reactions. Entropy is here interesting in that it serves as characteristic function in describing either equilibrium states and quasi-static ones, or irreversible processes. It permits consequently to study both these states within a unique thermodynamic approach. Equilibrium state is defined by the entropy's highest possible value, and entropy is the criterion of stability of an equilibrium state. In irreversible processes with matter flow through the system and a concentration gradient entropy is no criterion of stability insofar as it varies in time. This variation is composed of the flow of external energy and of entropy production in the reactions inside the system:

$$dS/dt = d_i S/dt + d_e S/dt \quad (4.2)$$

In relation to equation (4.1) the entropy flow is defined by

$$d_e S/dt = 1/T(dQ/dt) + \sum(dn/dt) \quad (4.3)$$

but the entropy production by

$$d_i S/dt = 1/T(dW/dt) + 1/T \sum A_r w_r \quad (4.4)$$

where $w = dn/dt$ is the chemical reaction's speed but $dS/dt = P$ is the variation speed (production) of the entropy. Contenting ourselves with the case of a constant level of energy of dissipation, supported from outside ($dw/dt = 0$), we get:

$$P = \sum A_r w_r \text{ et } dP/dt = 1/T d(\sum A_r w_r)/dt.$$

In stationary state $dP/dt = 0$, $d(\sum A_r w_r)/dt = 0$; $A_r \cdot dw_r/dt + w_r \cdot dA_r/dt = 0$, $A_r : dw_r = -(dA_r/dt) : (dw_r/dt)$. Admitting that t is the only independent variable, we can write $A_r : w_r = -dA_r : dw_r$. In the case of a linear relation:

$$w_r = a \cdot A_r, dw_r = a \cdot dA_r, dw_r/dA_r = -w_r/A_r = a \quad (4.5)$$

where "a" is a phenomenological coefficient, signifying in this case "facility" of initiating the corresponding chemical reaction: the greater "a" in absolute value, the less necessary the affinity to attain the same speed and eliminate the energetic barrier. For each reaction "a" is constant and a decrease of the reaction

speed brings about a proportional decrease of affinity. Since P possesses an additive value and $P_t = \sum P_r = \sum A_r w_r$, it is then necessary in order to initiate in parallel all possible reactions, to have higher affinity and speed and, consequently, a higher entropy production than the consecutive movement of these reactions. Consequently minimization of P requires a determined succession of reactions.

Formation of a mineral from an aqueous solution occurs in several stages: homogeneous reactions in the solution, formation of a crystal germ, growth of the crystal.

At the germination stage, synthesis of an active complex requires extra energy from an external source. Hence, the system's potential energy increases, accumulating in new interatomic linkages in the active complex, and entropy accordingly decreases because a supplementary structure appears. In this manner, at this stage, the system does not near equilibrium but moves away from it. This divergence, provoking kinetic effects, is mathematically expressed by violation of linear relations between chemical forces (reaction affinity) and flows (reaction speed). Reaction speed and chemical affinity are functions of T , P , C_i under the general form:

$$w_r = f_1(x_1, x_2, \dots, x_{n+1}); A_r = f_2(x_1, x_2, \dots, x_{n+1}) \quad (4.6)$$

Eliminating variable x_{n+1} we obtain:

$$w_r = f_1(x_1, x_2, \dots, x_n, A_r) \quad (4.7)$$

At equilibrium $A_r = 0$, $w_r = 0$. Since A_r is a measure of the divergence from equilibrium, we can put in row the expression of reaction speeds:

$$w_r = (df_1/dA_r)A_r + (d^2f_1/dA^2)A^2 + \dots \quad (4.8)$$

In close proximity of equilibrium (feeble value of A), limiting ourselves to the first term of the resolution, we get to (4.5): $w_r = aA_r$, where $a = (df/dA)$, the phenomenological coefficient. In future we shall omit the index "r" in the expression of the reaction's speed and affinity. Between reaction speed and affinity there is the relation:

$$w = w_f [1 - \exp(-A/RT)] \quad (4.9)$$

where w_f is the speed of direct reaction. In equilibrium $w = 0 = w_f$: for a divergence $0 < w < w_f$, but for a sudden irreversible reaction $w = w_f > 0$. In the following case, $1 - \exp(-A/RT) = 1$; $A/RT = \infty$, hence $A = \infty$. Therefore owing to the force of unbalanced processes, with a high value of A it is impossible to neglect the second term the resolution of the speed:

$$w = aA + (d^2f/dA^2)A^2 \quad (4.10)$$

which produces violation of linear relations between the speed of the reaction and its affinity. For constant concentrations of reagents, reaction speed is inversely proportional to the activation energy $r = f(\exp[-E^a])$, and the divergence from non-linearity in (4.10) is defined by E^a . Thus activity energy is the cause and simultaneously the measure of the system's divergence from equilibrium, a measure of its non-linearity. It may be considered the leading parameter, determining the process's path and speed. A specific speed of reaction (speed at unitary concentrations of reagents and products) is linked to this parameter by Arrhenius' correlation:

$$K = AkT/h \cdot \exp(-E^a/RT) \quad (4.11)$$

where A is the coefficient, K Boltzmann's constant, h Planck's constant, E^a the energy of activation.

As a result of the fact that the beginning of the reaction requires elimination of the energetic barrier, in the system at the stage of the crystal's germination there arise supersaturation on the reacting components and, consequently, at the limit of the reaction region, of the shading crystal with the remaining solution there must exist flows of matter and energy. In connection with the conditions examined above of a stationary state of the gradient system, the processes for obtaining such a state must obey the law of minimal production of entropy. Entropy production itself represents the speed of change of entropy and that is why it is a function of the speed of corresponding chemical reactions. Let us suppose for simplicity's sake (for simple reactions of the first order) that these values are linked to direct proportional dependence:

$$P = dS/dt = f(w_r) = qw_r = qk\Pi c_i \quad (4.12)$$

where q is the coefficient of proportionality. For unitary concentrations and for $k=1$, q equals "standard" production of entropy (P') and $P = P'w_r$. Supposing the components' concentrations to be maintained constant by an external flow we write:

$$P = P'k \exp(-E^a/RT) \quad (4.13a)$$

In the stationary state, entropy production is minimal.

$$dP/dt = 0 \quad \text{and} \quad dP/dt = P'kd[\exp(-E^a/RT)]/dt = 0 \quad (4.13b)$$

After integration from $t=0$ to the moment of formation of the active complex we get:

$$E^a/RT = \ln C \quad (4.14)$$

If the process is non-stationary, P is not minimal and in correlation with (4.13 a, b) the expression under exponent increases, i.e. the energy of activating the reactions, occurring for a higher P , is greater. This distinction is expressed in the various values of $\ln C$. When examining the real processes it is more correct to say that the states with a higher activation energy are characterized by a high entropy production and to signify they are instable and less advantageous as to energy. As we have shown above that formation of an active complex can be considered in the frame of the model of a system with gradients and flows to which Prigogine's theorem is applicable; then of all possible reactions with least activation energy it must not only start first but also occur in conditions nearest to a stationary state.

From that view-point, Ostwald's well-known rule is interpreted anew: if it is possible that in successive reactions for the reagent to be transformed into a final stable product, it is not a direct reaction that takes place but a formation of intermediate metastable products of which the free energies differ less from those of the reagent than do the free energies of the final product and reagents. Comparing this rule to the conclusion reached above, we may say that, as a rule, reactions with the least variation of free energy are characterized by the minimal entropy production. This is exemplified by a successive series of crystallization phases of silica from an oversaturated solution at low temperature; opal, cristobalite, tridymite, quartz. Values of free energy for minerals of this series equal accordingly (in Kcal/mol) -202,91; -204,17; -204,42; -204,71. As can be seen, energy value monotonously diminishes. Difference of energy is minimal for the pair opal- cristobalite and maximal for the pair opal-quartz. Succession in formation of silica phases, consequently, depends upon greater increase of the phases' free energy, although all precipitated phases, except quartz, are in low temperature conditions thermodynamically unstable. The system's option, by gradual, non trivial way of evolution (unlike the direct solution-quartz way) may be considered an element of auto-organization.

Usually, germ formation arises in the conditions of a non-stationary process, since the initial deep concentration overcooling rapidly decreases while the crystals start increasing and consequently conditions at the limit vary in course of time. However, constant repetition of successive metastable intermediate phases at formation of many minerals (silica form, polytypical micas and chlorites, structural modifications of alkaline feldspars, etc.) testifies to stability of the reactions' kinetics, i.e. to approach of stationary state. On low hydrothermal temperature synthesis of albite in experimentation and propylitisation processes is, as a rule, formed, at the beginning, "high" disordinate, albite, thermodynamically unstable at low temperature. Finally on it can be converted into its ordinate, low temperature stable form. Calculations

carried out on replacement reactions of plagioclase by albite show that the activation energy at the forming of metastable high albite constitutes 2.25 Kcal/mole at 1000°C, and that the stable ordinate form is 4.85Kcal/mole [Rusinov, 1972]. Consequently, the difference between the plagioclase' free energy (N°50) and the inordinate albite's is lower by a few Kcal than the ordinate albite's. Entropy increase is also smaller in the formation of inordinate albite and production of entropy is smaller for the processes of plagioclase – active complex – disordinate albite – ordinate albite, than in the row of plagioclase – active complex – ordinate albite. This confirms the hypothesis that the process tends to a stationary state, choosing a gradual path towards equilibrium through metastable phases. Interestingly, with temperature increasing, the degree of ordination of albite forming in natural processes increases, and above 350°C perfectly ordinate albites are formed. Evidently with temperature increase the energetic threshold decreases and so does the solution's saturation degree and it means that the reaction's chemical affinity of inordinate albite formation diminishes. Inasmuch as crystallization of ordinate albite begins, the corresponding speed of synthesis of inordinate albite decreases. Consequently we approximately observe the correlation of proportionality $A = ar$, for which, as shown above, the principle of minimal entropy production is justified. It means that the process nears a stationary state.

Analogous calcifications lead to a similar conclusion, and for the formation of dioctahedric polytypes of bright micas in the synthesis of which, at temperatures of 200-300°C metastable polytypical modification 1 M occurs first, activation energy for their formation being lower than for stable modification 2M1[Mukhamed-Galeev & Zotov, 1989].

Kinetics of metasomatic reactions also exerts an influence on the metasomatic zoning structure, now little significant, now essential. We examine D.S.Korzhinsky's basic equation of infiltration metasomatic zoning. It is based on the relation:

$$(dC/dx):(di/dv) = -1/f = K$$

Further on, he calls x and v a single variable, which tallies with an accepted assumption about attainment of local equilibrium and invariance therefore of spatio-temporal coordinates. If then we consider the speed of chemical reactions as a non-instantaneous but final value (as happens in reality), parameters x and v are found independent and cannot be replaced by one. Inside each zone, where equilibrium exists between rock and solution, there is no variation in the content of components in the rock and in the solution ($dC_i = di = 0$). At the zone limits these changes have the final value $(\Delta C_i/\Delta i)/(\Delta x/\Delta v) = K$, where x is the distance from the section where the chemical reactions begins, v the volume of the solution percolating through the section in course of time from the initial to the given moment. Taking into account that $C\Delta V = \Delta M$, i.e. the component a 's variation of mass in the solution, and that M in the time unit

represents the reaction speed ($\Delta M = r$), then $r/\Delta i = K/\Delta x$. As far as, for a constant temperature, one can adopt a reaction speed almost constant one can write $x\Delta i = K'$, i.e. with moving from the initial section towards direct percolation of the solution, the component i 's content in the rock varies according to a hyperbolic law (fig.4.2a) and the component's distribution profile in the rock in the three – zone – column must look (as shown on fig. 4.2b) (right angles attenuated by diffusion).

If we fix the component's content in the rock (i.e. the section's position in space), then $C\Delta v = K''$ or (since Δv is function of time) $C\Delta t = K'''$. Concentration variation in course of time also follows a hyperbolic law.

Influence of speed of chemical reactions on the form of limits between zones in the column of metasomatic zoning is in many cases insignificant. In experiments with small zones and transverse section of the solution flow, it is most often unobserved [Zaraisky, 1991]. However, in natural objects this influence is frequently an important factor. In particular, in the systems with participation of iron, manganese and other elements with valence changes, the determined (critical) correlation of the speeds of chemical reactions (including oxydo-reducing reactions in the solution), may result in stability loss of the thermodynamic path of the zoning's development. In such cases there appears in the solution a dissipative structure, which is reflected in a rythmico – ribboned zoning in the rock.

In low temperature processes reaction kinetics determines dissolution sequence of the rock's initial minerals and influences the forming of associations of minerals and metasomatic zoning. In the hydrothermal changes of recent volcanic thicknesses are formed rocks composed internally of mineral associations in unbalance [Rusinov, 1972]. As a result a complex metasomatic zoning has formed, including a zoning newly formed as a whole of minerals in equilibrium with the solution's composition, as well as relicts of magmatic minerals. The latter's dissolution follows a rigorous sequence, characteristic of the determined interval of temperature and the hydrothermal type. On propylitisation olivine and hypersthene are dissolved in the most external zone; near the internal ones have successively dissolved augite, plagioclase, hornblende, magnetite. This succession, permanent with weak variations for physico – chemical conditions determined in various geological environments has been called "dissolubility row". Unlike this row is one characterized by of middle temperature processes, linked for instance with metamorphism of green rock metamorphism. In these conditions, plagioclase and albite change places with a row of solubilities: plagioclase dissolves totally and is replaced by albite in a first stage, while augite remains unchanged even in intensely metamorphosed rocks. Observations in regions of active volcanism have shown that dissolution speed of plagioclase rapidly increases as temperature grows from 100 to 300°C, while the speed of augite dissolution slowly grows.

Reaction speed for fixed concentrations of components and temperature is defined by activation energy $A \exp(-E/RT) \prod_i C_i^{\nu_i}$.

Supposing $\prod_i C_i^{\nu_i}$, A and E constant after passing to logarithms and differentiating we obtain $d \ln K = -(E/RT^2) dT$. After integrating in the interval from T_1 to T_2 (correspondingly from K_1 to K_2 , making $T_2 - T_1 = \Delta T$) we get the hyperbole equation [Rusinov, 1972] $(E + \Delta E)(\ln[K_2/K_1] - E/RT) = -E/R$. In the coordinates $T - \ln[K_2/K_1]$, the hyperbole is situated in the second and fourth quadrants (fig.4.3). The steep curve in the realm of low temperatures depends upon the coefficient in the equation: the greater E/RT_1 the quicker varies the reaction's specific speed with temperature increase.

In the example examined above, at low temperature the plagioclase's dissolution speed is smaller than the augite's, but at higher temperature the relation is inverted. Evidently this is provoked by a greater energy of dissolution activation of the plagioclase compared to that of augite. The order of dissolution of residual minerals determines in the solutions gradual dissolving of such and such component and therefore influences the order of precipitation of the newly formed minerals and the zoning of their distribution. This influence is observed in the external zones of shallow propylites [Rusinov, 1972]. Near the internal zones, residual minerals undergo complete dissolution, and zoning approaches the one theoretically expected. It is curious that the order of dissolubility treated above (the order of increase of the minerals' activation energy of dissolution) for low temperature metasomatism tallies with the successive decrease value of entropy and enthalpy of these same minerals in standard conditions.

In this way kinetic relations may be used in interpreting mineralogical associations, although great difficulties remain in creating general theories on mineralogical associations in unbalance: there is a deficiency of experimentally determined kinetic constants and the data's fragmentariness about links between kinetic and thermodynamic parameters. More promising is the use of the kinetic approach, the study of auto-organized phenomena in systems in unbalance.

4.3. Self-organization and synergetics of metasomatic systems

A metasomatic system is an example of a complex dynamic system in which side by side with progressive movements of aqueous solution flows through a porous environment, a whole series of chemical reactions takes place between solution and rock. A system difficult to modelize because in it a dynamic flow is combined with chemical interactions, and side by side with signs of equilibrium between rock and solution, in an infinitely small volume there occurs a manifest unbalance at the limits of zones where replacement reactions take place. Moreover, metasomatic zoning testifies to structuration (structure condition) of a petrological system in which chemical reactions do not take place in the whole volume of replaced rock but are concentrated on discrete

regions, at the replacement fronts. Naturally the zoning's theoretical modeling was made by way of approximation of the process through simpler physico-chemical models based on the thermodynamics of locally stable states (cf. Chap.2) or on kinetics of chemical reactions towards obtaining equilibrium between rock and solution. However, such models have proved not capable to interpret arising structures more complex than those in equilibrium, and resulting from a system's auto-organization [Klimontovich, 1995].

The most widely spread aspects of complex structures appearing in rocks due to autoorganization phenomena, are rhythmical, ribboned structures (linear and concentrically zonal), torch-like, globular structures and some others. Their appearance is conditioned by Belousov-Zhabotinsky's (dissipative structures) either by oxido-reducing oscillating chemical reactions or by an autocatalytic mechanism and the reaction's evolution in a regime of exacerbation. General conditions of appearance of auto-organization in a physico-chemical system are: a strong unbalance, appearance of inverse linkages between elements of the system, influence of chemical kinetics with which is linked the process's non-linearity. The basic tenets of the auto-organization theory are in conformity with geological systems, and partly with mineralogical ones, and examples of such systems are contained in the books of F.A.Letnikov [1993] and P.Ortoleva [1994]. A few partial models of metasomatic systems are examined in articles by Russinov & Zhukov [Russinov *et al.*, 1994, Russinov & Zhukov, 1994].

In the basis of the theory of metasomatic systems and processes is included the theory of metasomatic zoning. Its first mathematical model was given by D.S.Korzhinsky, who considered metasomatic zoning as an indispensable attribute and typical sign of metasomatic processes, distinguishing them from magmatic and metamorphic ones. The mathematical models of diffusion and infiltration zoning he has elaborated (cf.chap.3) are based on the principle of local equilibrium and suppose formation of sharp, uninterrupted limits between zones and between an external zone and the immutable rock. At the limits (fronts) there occur chemical reactions with replacement (or dissolution) of one of the minerals of the most external zone and a jump of concentration or chemical potential of a corresponding component in the solution. Models were initially applied to processes of skarn formation, then to greisens and other objects and have shown a better correlation between them. Later on the model of local equilibrium was confirmed by theoretical and experimental researches [Zaraisky 1989, Balashov, 1985].

In low temperature processes a zoning's formation is complicated by kinetic effects owing to weak speed of chemical reactions. Studying these effects, V.S.Golubev [1981] has obtained systems of dynamic and kinetic equations, describing the components' distribution in the solution flow and in the rock with which it reacts, a distribution depending not only upon initial and limit conditions, but also upon time. The obtained kinetic equations show the

possibility of progressive variation of quantitative correlations of minerals in the zones of the metasomatic column, in case of influence of chemical kinetics.

Further development of the theory of metasomatic zoning is linked to study of strongly unbalanced processes, in which auto-organization is manifest. Auto-organization can only arise in open systems [Prigogine, 1985] at an exchange of energy and mass with the environment, i.e. under external influence. For a weak value of the external influence, usually designated by the term controlling parameter (which evokes variations in the system and its passage from equilibrium to unbalance) fluctuations arising in the system vanish, and it returns to equilibrium. When this parameter increases, fluctuations are stabilized and may increase, but when it exceeds a critical value the system passes to an auto-organization regime.

Schematically it can be shown on a bifurcation diagram that the model of local chemical equilibrium tallies with the stable state for which the controlling parameter's value is equal to zero. V.S.Golubev's kinetic model encloses the interval of the controlling parameter's small values (the kinetic realm of the linear correlations of forces and flows) but at the bifurcation point, is settled the domain of synergetic effects (Fig. 4.4). G.Haken [1980] has called synergetic the directive, current among scientists, which analyses synchronic or cooperative action of the system's components resulting from auto-organization and fractality (self-similarity) of the systems. Synergetic effects (autoorganization) in metasomatic processes appear in 1) structure and dynamics of the front of introduction of the metasomatizing solution into the rock, instability of a flat front and appearance of clusters of percolation (penetration). 2) conditions of percolation of running waves of concentration and formation of rhythmico-ribboned (periodical)zoning. 3) some fractal properties of metasomatic zoning.

Autoorganization in the solution's filtration flow appears at once at its entering the rock. A metasomatic system is heterogeneous and strongly unbalanced. It consists of a porous rock, an intergranular solution in equilibrium with the rock, and an extraneous solution from outside into the porous space and in unbalance with the rock and the inter-granular solution. The introduced solution is generally characterized by physico-chemical parameters different from those of the inter-granular solution. In particular, it has another density and viscosity due to difference of temperature and salinity. Therefore both solutions may be considered independent phases, at least in the zone of the foremost metasomatic front. Their dynamic interaction determines to a large extent morphology and some other features of developed zoning.

The normal succession of fronts, i.e. of interzonal limits is the skeleton of metasomatic zoning. Some morphologic varieties of such reaction fronts for simple cases of directional zoning are considered in the works of P.Ortoleva [1994]. The most interesting case is that of a "trapping" front with precipitation

of a “reactional” (Korzhinsky’s term) mineral, since it leads to formation of metalliferous concentrations, for example uranium mineralisation at the dissolution front of the initial rock (Fig. 4.5).

A plane continuous front of advance of a solution in a homogeneous porous environment with dissolution or replacement of its minerals is stable only for a relatively weak filtration speed. On its increase beyond the critical value it loses the stability of the already relatively weak heterogeneities of the rock at grain level. Consequently salients are formed in them that do not disappear in course of time but stabilize themselves and tend to increase (Fig. 4.6). This phenomenon, known as fingering, is a typical example of autoorganization [Ortoleva, 1994]: the solution retreats to the salients’ basis from the flow’s neighboring strips; the salient growth accelerates, but that of the contiguous hollows slows down. On studying the calcite’s dissolution it appeared that along the salient’s wall convective flows are formed, additionally feeding the salient with fresh solution. In the growth process, depending upon the relative filtration speeds, the salient’s structure may get complicate. It may tend to ramify (Fig. 4.6).

The plane front’s instability is the basis of formation of clusters when the solutions’ flow filtrates. The solution’s introduction takes place in a system of pores along limits of the mineral grains. In the case of compact (volcanic, intrusive or metamorphic) rocks the solution’s fundamental mass may be considered as propagating at the inter-granular limits. Thickness of gap between grains in arbitrary sections is infinitely less than the separating surface. Therefore the solution’s movement may be approximate to the one in a bi-dimensional space. Then, analysis of the conditions of introduction of the metasomatizing solution in the rock comes down to a bi-dimensional problem of displacement of one liquid phase by another from the intergranular space. The solution of this problem from the general standpoint and from that of mathematical modelizing for a different relation between the two phases’ viscosity [Panfilov & Panfilova, 1996] shows that introduction occurs along a net of percolation clusters. On Fig. 4.7 can be seen an example of a tri-dimensional computer model of percolation clusters. The latter’s character is defined by a relation between viscosity and speed of the infiltrating solution but the shape is similar to a multi-ramified net of filaments or dendrites. The dendritic clusters’ morphology varies depending upon correlation of viscosity of the displacing and displaced phase and upon filtration speed. If the viscosity of the displacing phase is smaller than that of the displaced one, for instance because of high temperature and low salinity, there are formed jets of rupture with small transversal branches. A continuous front is lacking. The whole structure is lengthened towards the pressure difference. Consequently there remains in the rock “enclaves” (unreplaced parts) and the front zone of the metasomatic zoning is a system of more or less oriented veins. Such stockwerks

composed of a net of ramified metasomatic subvertical veins, made up of carbonates, quartz, epidote or biotite, are rather common in the aureoles of deposits of some auriferous hydrothermal veins. If the displacing phase's viscosity exceeds that of the displaced one we are near such a situation, but at the same time there forms behind the clusters a continuous substitution front. An increased role of capillary forces furthers the clusters' ramification and a more complete filling up of the space with a cluster.

The described clusters are self-similar, i.e. the structure of part of a cluster on whatever scale is similar to that of the whole. The degree of self-similarity (fractality) valued by the fractal dimension, for clusters of displacement of liquid by gas (calculated for displacement of petrol by gas) varies between 1.3 and 1.7 and is close to the universal value of the plane clusters: 1.71 [Panfilov & Panfilova 1996]. Appearance of such a scale of invariance is possible on condition there exists in the system a link of remote order and reverse links between its parts. In that sense it can be said that fractalization serves as sign of the system's synergy, and the fractal dimension as measure of its degree.

It was noted above that metasomatism takes place with the participation of aqueous solution in unbalance with the rock. The solution infiltrates the rock through a net of fractures and zones accompanying the solution. Admitting the fractures' breadth to be negligible compared to their expanse they may be considered topologically a bi-dimensional, i.e. superficial object. In the direction of the solution's movement these channels align themselves in a definite succession. In the first place the solution propagates through large fractures to great length, from which it infiltrates in the form of percolation clusters in smaller fractures, from which it spreads along the limits of heterogeneity within the rock and further in intergranular limits and intragranular fractures. In space, the aggregate of these channels forms a net of successive ramifications from a main trunk resembling the crown of a tree (the development of a portion of the solution is represented on Fig. 4.8). There is a more precise analogy with the system of blood vessels of living beings, which distributes blood to each cell of the whole organism. In this way the solution as a result of innumerable ramifications invades each grain of the rock, filling up its whole volume. As a result, the fracture system and the limit of heterogeneity in the rock, forming superficial ramifications, fills up the volume, i.e. acquires the property of a tri-dimensional object. This surface becomes fractal and possesses a fractal dimension $2 < D_{fr} < 3$ [Mandelbrot, 1982], distinguished from the topological (cartesian) dimension of the surface ($D_t = 2$), as well as from the tridimensional objects ($D_t = 3$). One can calculate the value of the dimension D_{fr} for each concrete system, calculate the number of ramifications at each step on a length of several steps (generations of ramification) or calculate the area of spatial

filling while changing the scale of count. For the surface's projection represented on the plane of the sketch on Fig. 4.8, $D_{fr} = 2.58$.

In G.Wagner's [Wagner, 1997] experiments the liquid is displaced from the space between two loosely pressed glass blades by means of blown air. The clusters in this experiment look like bubbles united by microporous conductors. Also possible is a full disengagement of these air bubbles from the feeding zone. The bubbles distribution according to dimension in the experiment had a fractal character, i.e. the dependence of the number of bubbles of a determined dimension upon their diameter was gradual.

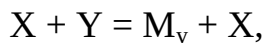
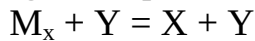
$N = r^{-D}$, where D is the fractal number and, in case of plane clusters, $1 < D < 2$. In case of formation of clusters with such a morphology (bubbles) through a reciprocal chemical action of the solution's forepart with the rock, metasomatic nodules arise or ovoids of newly formed minerals, as if the metasomatic fronts were not linked to those, complete, that follow them. G.L.Pospelov has described similar formations. These are linked, evidently, with nest biotitization surrounding cupolas of continuous biotitization in the gold deposits of Muruntay (Fig. 4.9). Fig. 4.10 shows a photo and a sketch of part of the argentiferous epithermal veins of the Dukat deposit. A zone of continuous bertierinization (chloritization) is bordered by one of rhythmical ribboning of an adular-bertierite aggregate, and between them are settled zones of ovoids of the same composition with an adular nucleus.

The formation mechanism of rhythmical ribboned skarns with wollastonite-hedenbergite has been examined (Fig.4.11). The photo shows fractalization of such a rhythm system. The succession of alternating finer and coarser stripes changes from place to place in the zones, but in certain the intervals the fractal dimension nears that of Kantor's quantity, 0.45. Consequently the given system is an example of auto-organization of a hydrothermal metasomatic process, complicated by repeated changes of trajectory in course of evolution. Models of rhythmic zoning in some particular cases were earlier on examined by V.V.Zhukov [Rusinov & Zhukov, 1994].

As the most general model, obtained as case of local equilibrium as well as of processes of extreme unbalance, appears a model of metasomatic zoning of isothermal filtration on a basis of running fronts and waves. Research of the system of dynamic and kinetic equations and the character of their solutions have shown that replacement fronts may vary at a constant speed, become sharp and tally with D.S.Korzhinsky's model of local equilibrium. Frequently, however, the replacement front is not a bi-dimensional surface but has a certain thickness due to the final value of the speed of replacement reaction. Then waves of concentration may appear. With the statements about running waves according to a regular initial distribution of the component in the rock, we come back to the model of running fronts and local equilibrium. In this case the rest point of the system on the phase surface proves unattractive. It is an unstable

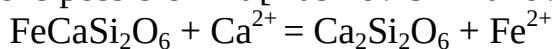
saddle with separate trajectories, therefore there can be here no oscillations. But if distribution is heterogeneous, one or several waves may appear, but in this case there is no stable oscillatory regime.

Most interesting is the case of oxydo-reducing reactions in the solution. They notably serve as starting point of the system's oscillatory regime of functioning. Let us examine the system with ions of oxydo-reducing iron or from a general point of view, of whatever element of variable valence

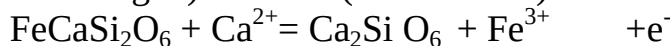


where X is the reduced form, Y the oxydated one, M are the minerals. As a result of research on the stability of resolution tallying with the equations of reaction speeds were obtained phase portraits of the system for the considered variants (Fig.4.12). From all these possible variants only an unstable focus can initiate an evolution along a stable closed trajectory of a limited cycle type and consequently arouse stable space oscillation of concentration. Observed rhythmico-ribboned rock structure represents a copy of dissipative structure developing in the solution. Fig. 4.13 shows the result of numerical modeling for skarns with wollastonite-hedenbergite and it is visible that the development of stripes of enriched minerals loses touch in course of time from the evolution of dissipative structures in the solution.

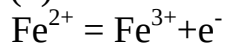
Petrographic research has allowed to establish that rhythmic zoning has appeared there as a result of a two-stage process. At first was formed on limestone a wollastonite skarn with uniformly scattered grains of hedenbergite with magnesium and aluminum, and later on there was dissolution of this early hedenbergite and precipitation of much later hedenbergite highly rich in iron and void of aluminum in the form of thin stripes within predominating wollastonite. Dynamic and kinetic analysis of the system is based on equations of the main reactions possible in it [Rusinov & Zhukov, 1994].



(1)



(2)



(3)

Moreover, account has been taken of the existence, in the solution, of mono- and poly-nuclear iron complexes. Analysis of the relation of speeds of direct and inverse reactions in the system, with simultaneous analysis of the dynamic equations of the solution's filtration, has shown that the described rhythmico-ribboned structure is formed in two stages. At first, dissipative structure appears in the solution with an undulatory distribution of concentration of bivalent and trivalent iron. Then it evolves and provokes dissolution and

peripheral deposits in form of stripes. This class of dissipative structures results from oxydo-restoring reactions, both homogeneous in the solution and heterogeneous between solution and minerals.

From the standpoint of the examined mechanism the conceptual coincidence of periodical zoning usually occurs to a forward zone of the metasomatic zoning as forming in the system's most tense unbalanced regions. We are thus not far from exhausting the reserve of the metasomatic zoning's synergetic properties, perspectives for further research.

In this way, autoorganization in its various forms of appearance is a characteristic property of metasomatic and hydrothermal metalliferous systems, and its research presents itself as of both theoretical and practical interest.

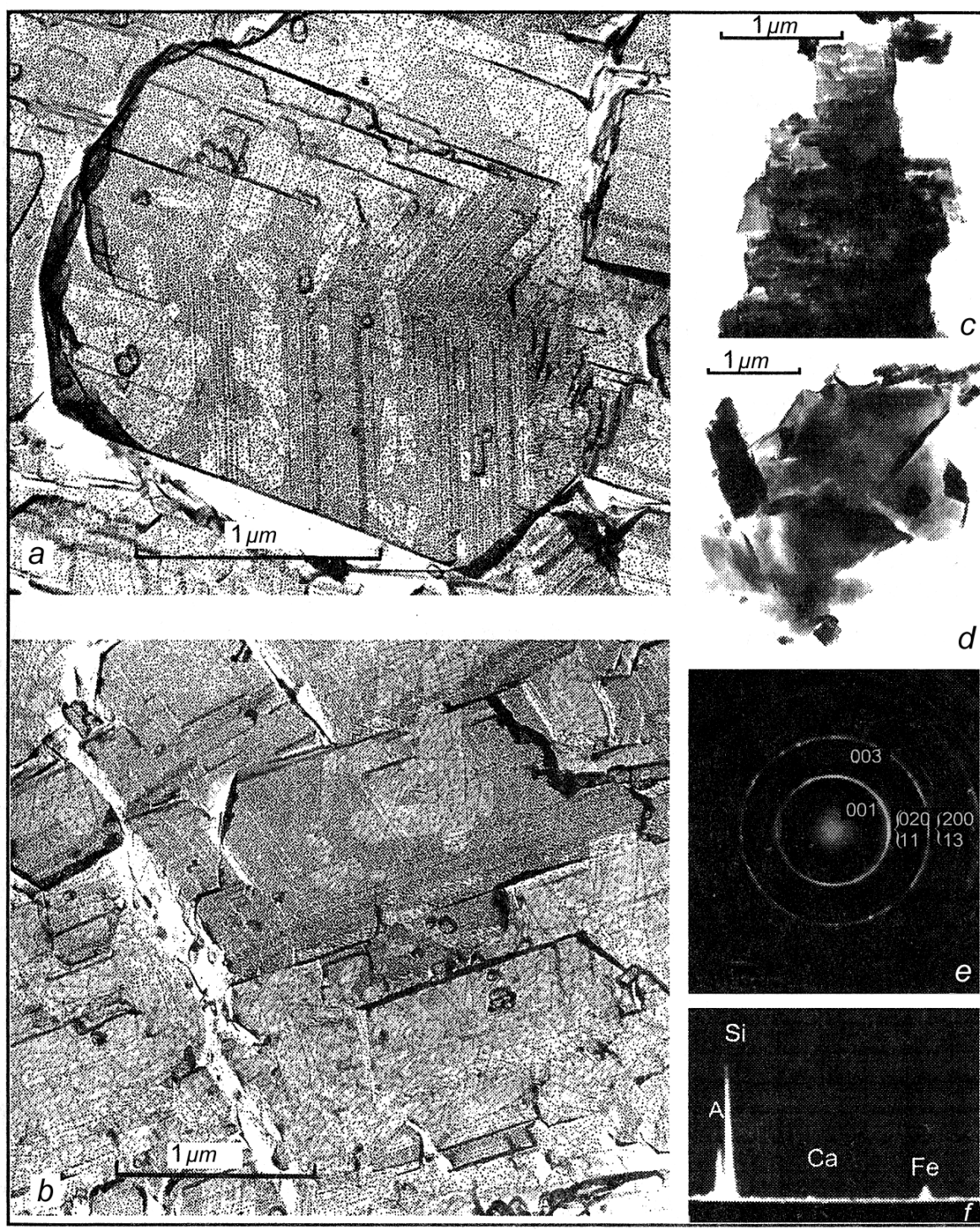


Fig.4.1 Electronmicroscope photo of gold-pulverized sanidine crystals and its surface replacement by montmorillonite according to [Samotoin et al., 1996]

a,b - photos of pulverized surface of sanidine; c - photos in parallel light (c, dissolved grain of sanidine, d, newly formed montmorillonite), e, microdiffractogram of montmorillonite; f, its spectrum of energy dispersion.

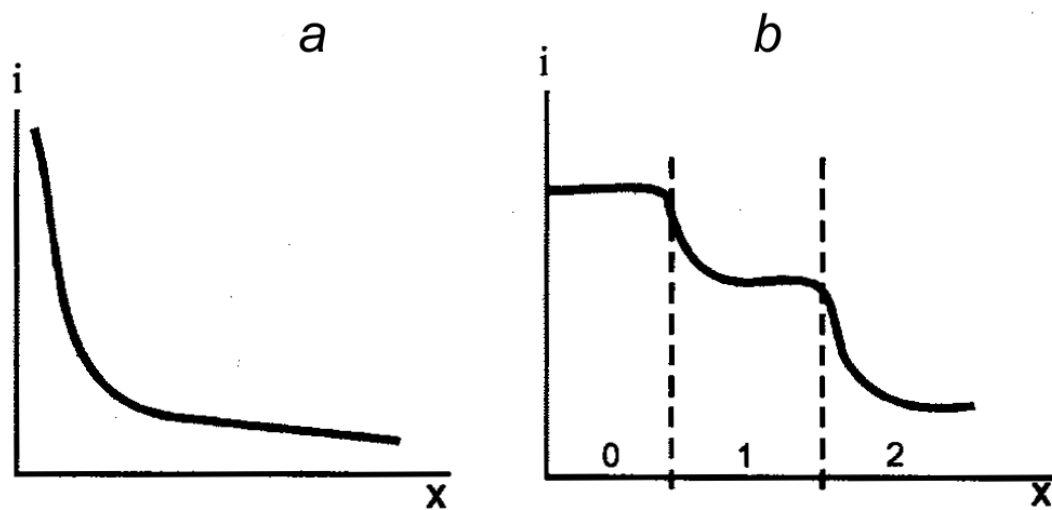


Fig.4.2 Dependence of component's content in the rock upon distance (x) towards the percolating solution (a) and also for the column (b) composed of three zones

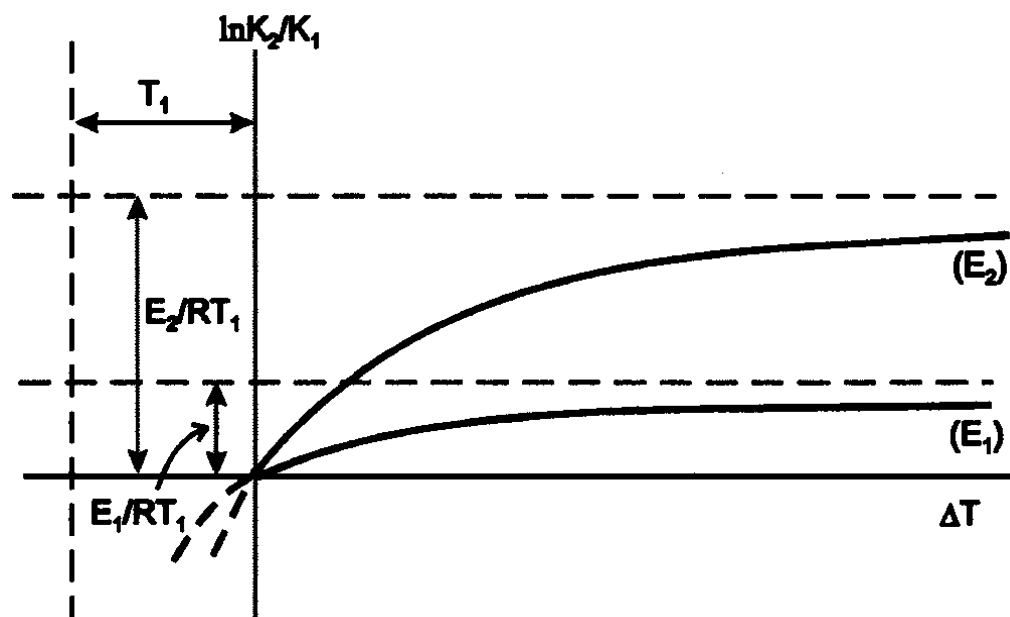


Fig.4.3 Dependence of speed variation of activated energy of chemical reaction upon increase of temperature, after [Rusinov, 1972].

K is constant of reaction , E is activation energy.

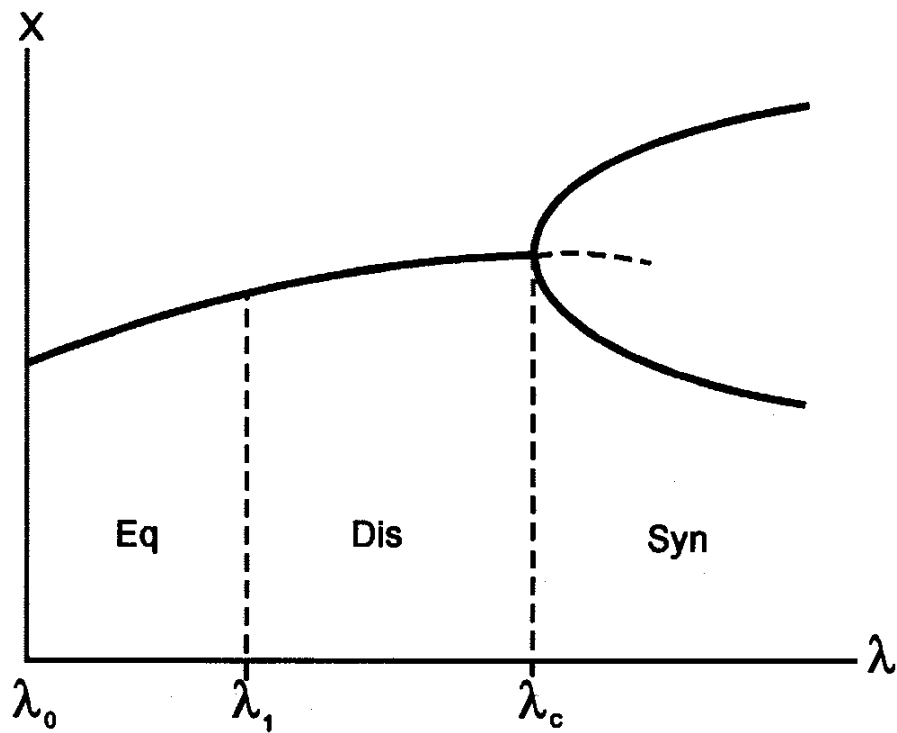


Fig.4.4 Bifurcation diagram.

X is propriety of the system (concentration, density etc.); λ simplifying parameter (λ_0 - equilibrium, λ_1 -unstable linear correlation, λ_c - critical point or point of bifurcation). Eq - area of linear correlations, close to equilibrium; Dis - unbalanced area of non-linearity; Syn - open area of synergetic effects.

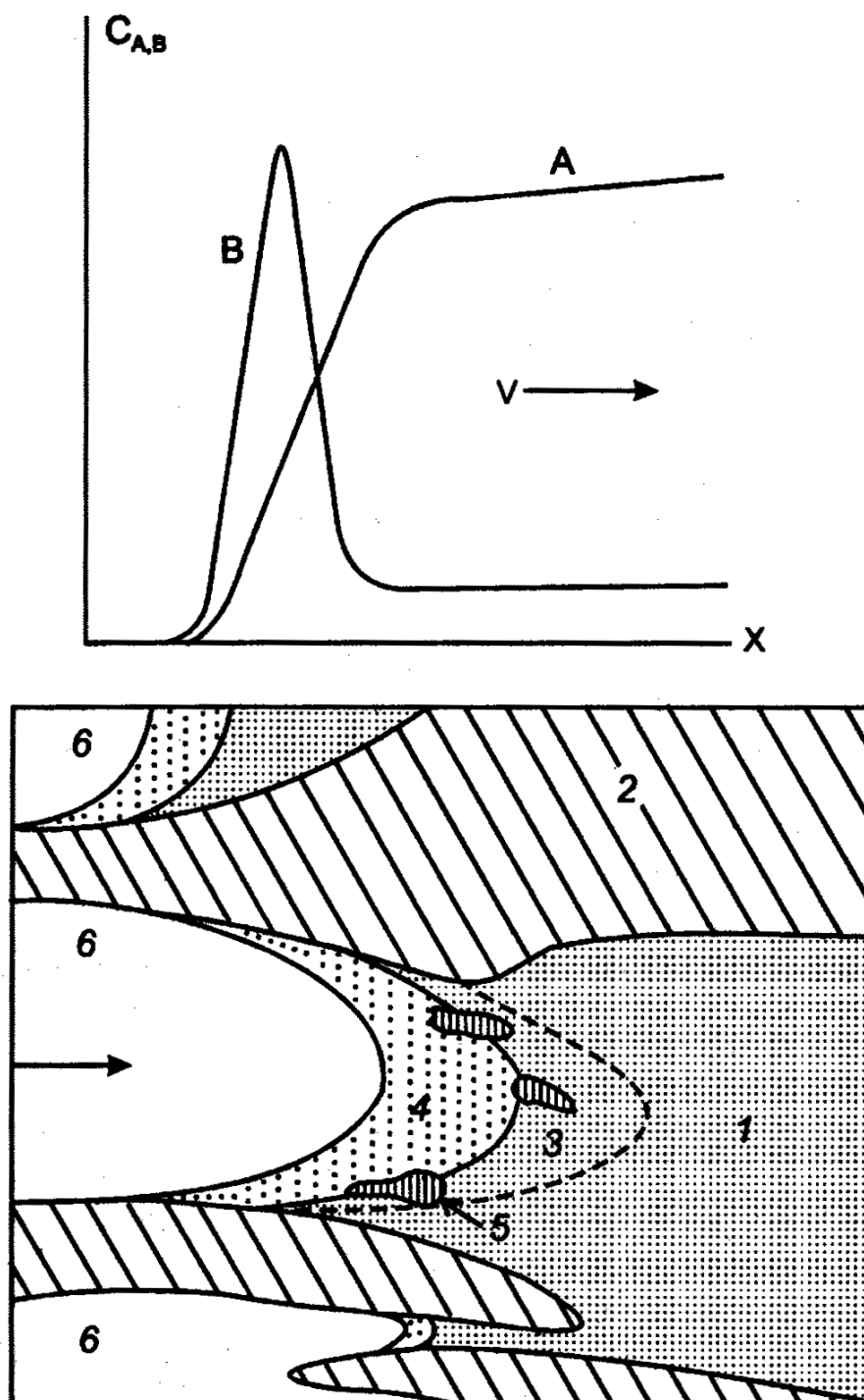


Fig. 4.5. Above: schema of structure of a forced front of precipitation of mineral B on the front of dissolution of mineral A (the arrow indicate the direction of filtration of solution). Below: schema of formation of uranium deposit in front of dissolution of sandstone by a metalliferous solution [Ortoleva, 1994].

1 – sandstone; 2 – zone of pyrite dissemination; 3 – zone of intense pyritization; 4 – zone of uranium ore; 5 – zone of calcite concretion; 6 – zone of argillisation; arrow indicates direction of filtration of the solutions.

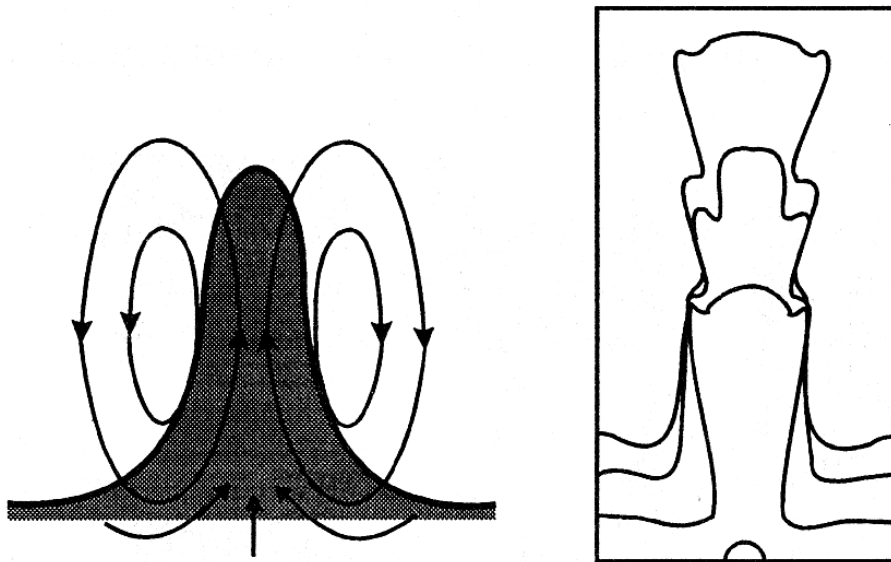


Fig. 4.6. Formation of plumes owing to unstable movement of flat fronts (left). Arrows indicate direction of movement of solution and matter transfer. Right, complications of structure of plume in the course of its growth.

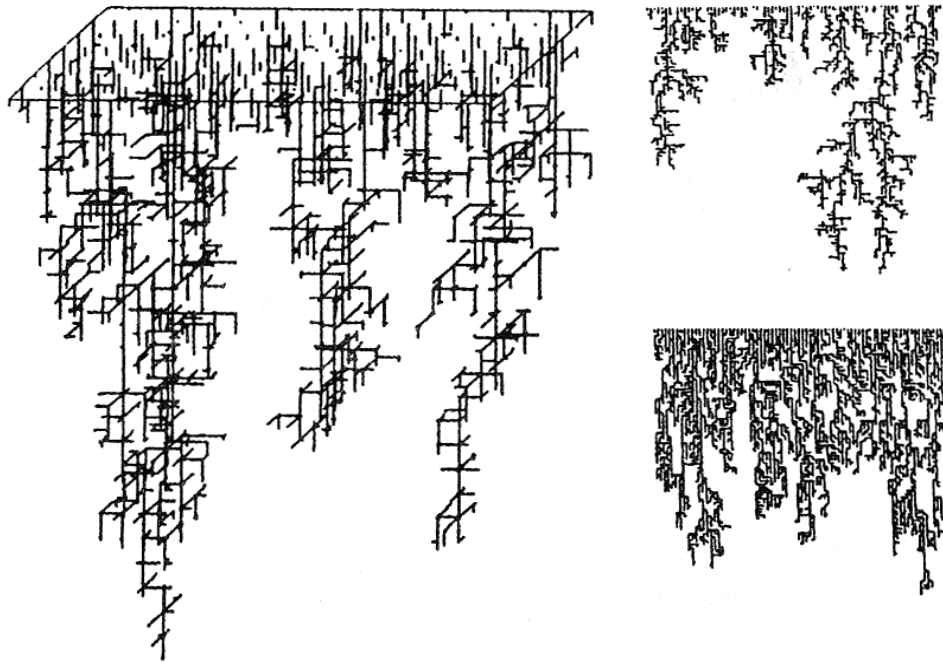


Fig. 4.7. Result of numerical modelisation of percolating clusters after [Panfilov & Panfilova, 1996].

Left, tridimensional model; right, bidimensional clusters of displacement of more and less viscous liquid.

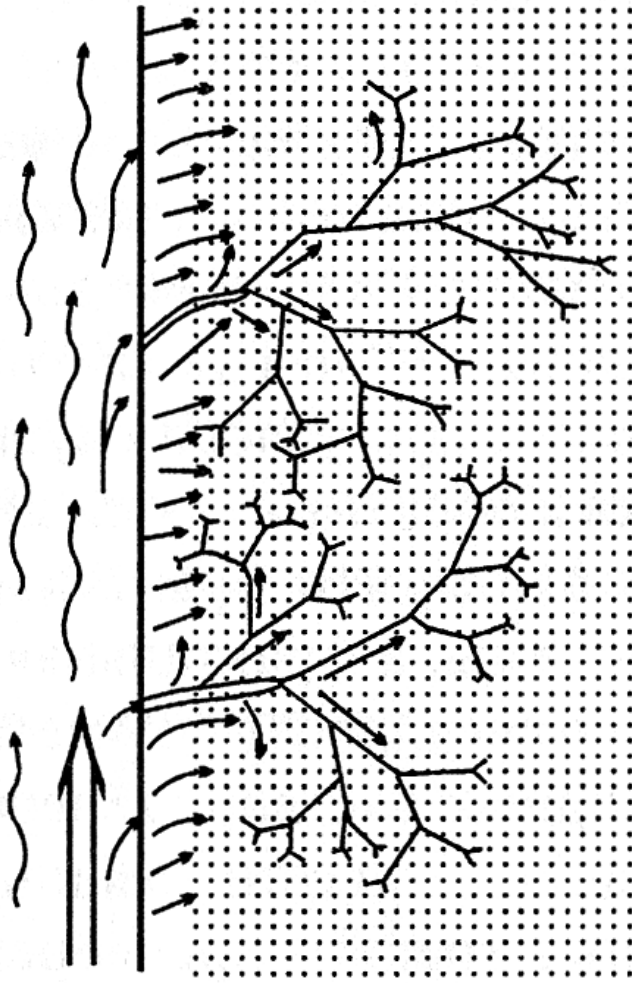


Fig. 4.8. Forms of solution arising from an open fissure in uniformly cracked and porous lateral rock.

Arrows indicate direction of solution's movement.

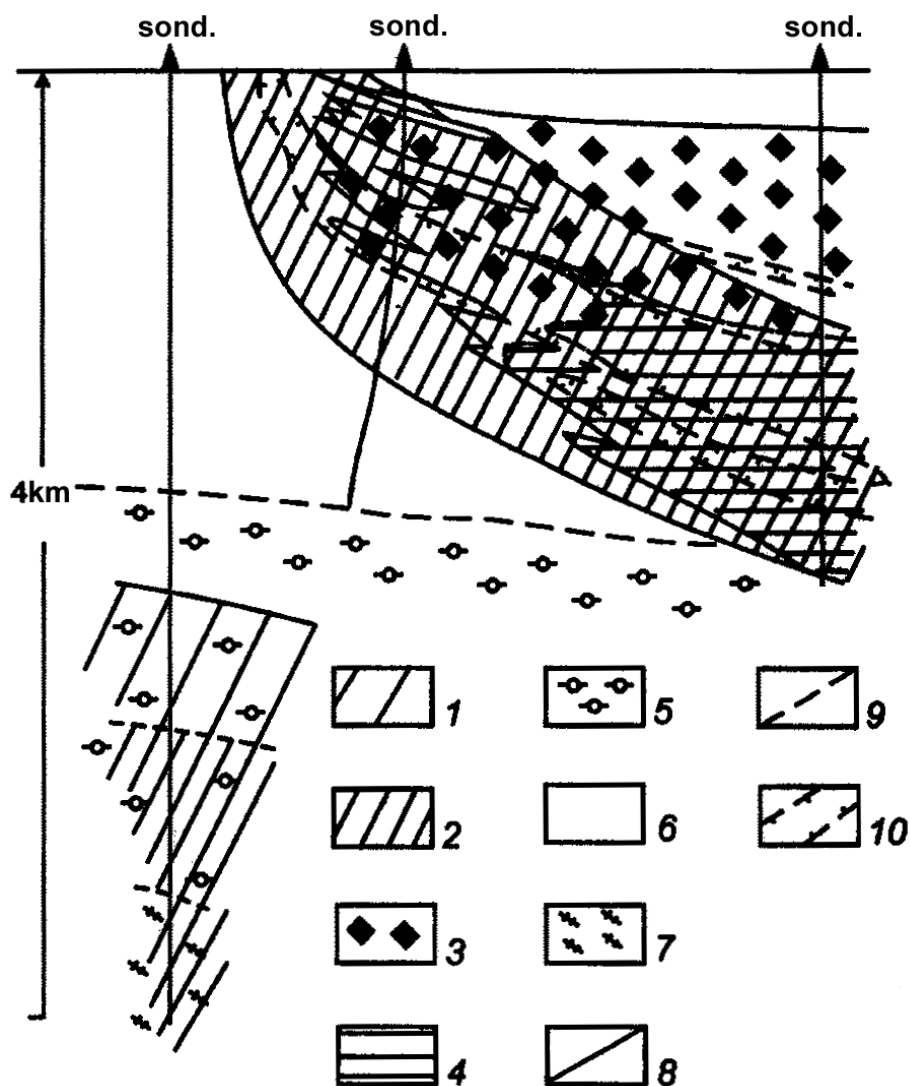


Fig. 4.9. Extent of metasomatic rocks in a section through part of ore-field of Muruntay after [Rusinov & Rusinova, 1998].

1, 2 - zone of skarns association (1 - antinolite facies, 2 - pyroxeno-clinozoisite facies); 3 - zone of "insular" biotites hornfels; 4 - zone of micahornfels; 5 - cupola of early biotites; 6 - enclosing schists; 7 - area of granite injection; 8 - boundaries of facies; 9 - boundaries of subfacies; 10 - boundaries of extent of ore mineralisation.

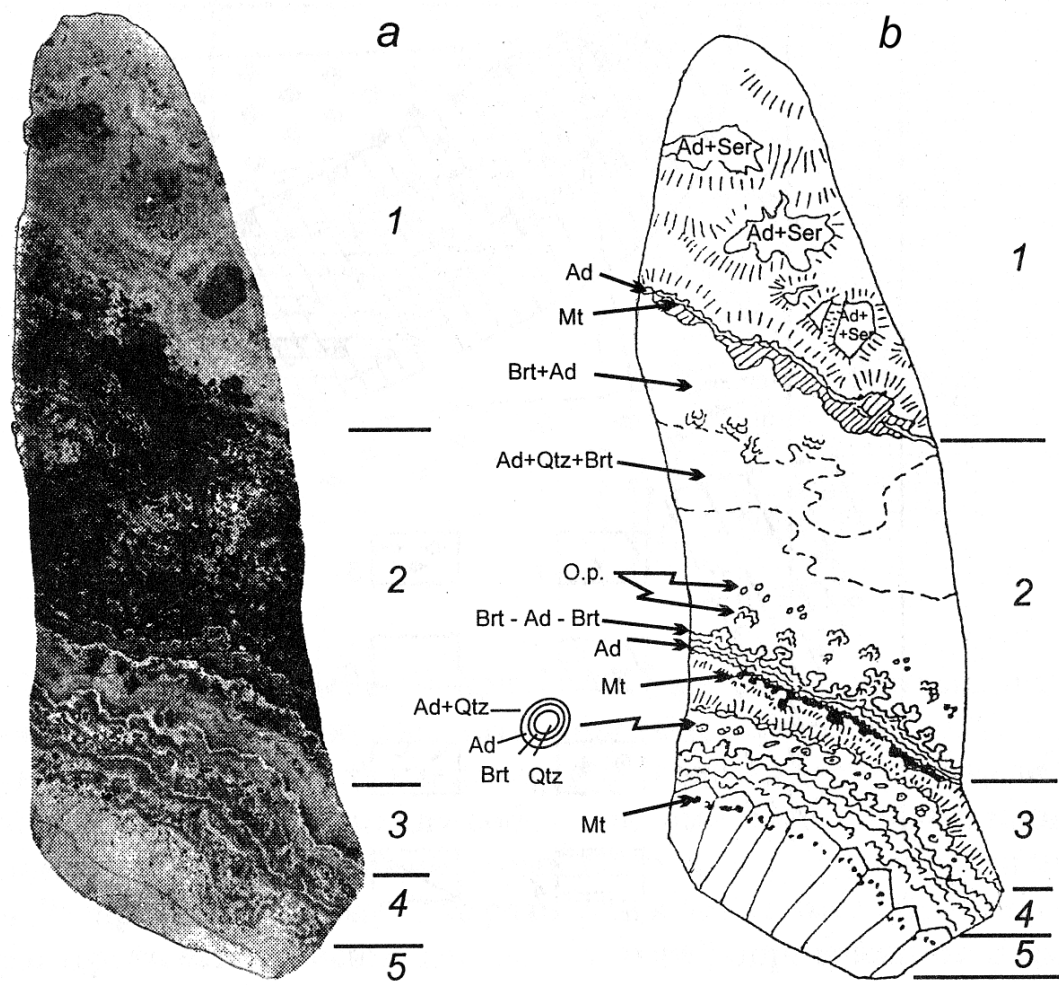


Fig. 4.10. Photo (a) and design (b) of sample from quartz-ore vein from gold-silver deposit of Dukat (Okhotsk – Chukotsk volcanic zone). Samples from collection of V.V.Krylov.

Digits indicate metasomatic zones; o.r. shows insular rhythmical bertierite-adular. Length of sample 30 cm.

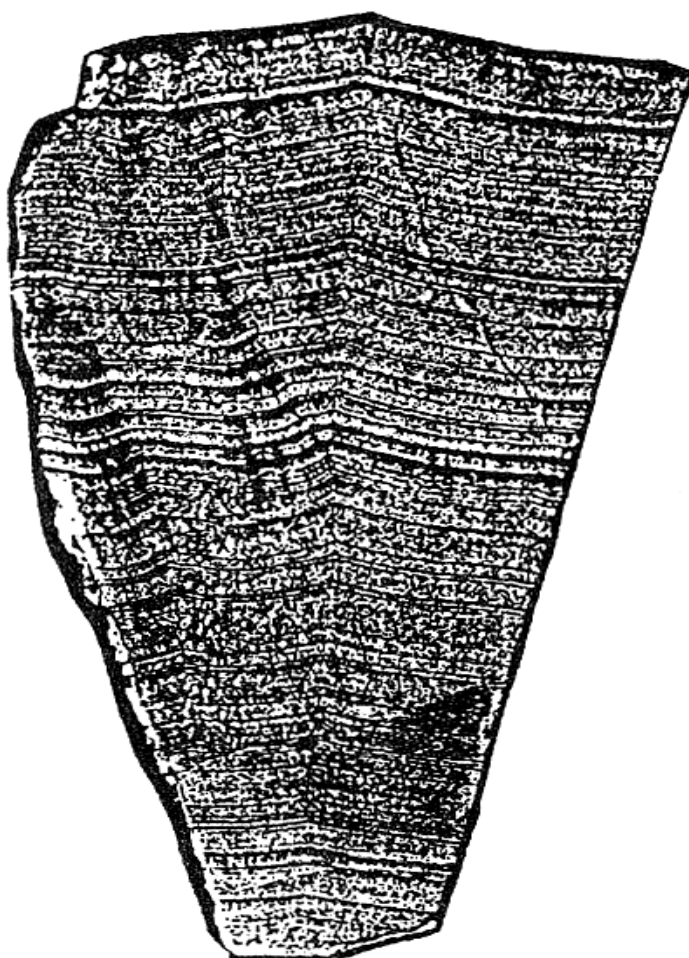


Fig. 4.11. Photo of sample of rhythmically banded wollastonite-hedenbergite skarn from boron deposit of Dalnegorsk (Primorie).

Dark stripe, hedenbergite, digit stripe, wollastonite. Length of sample 18 cm.

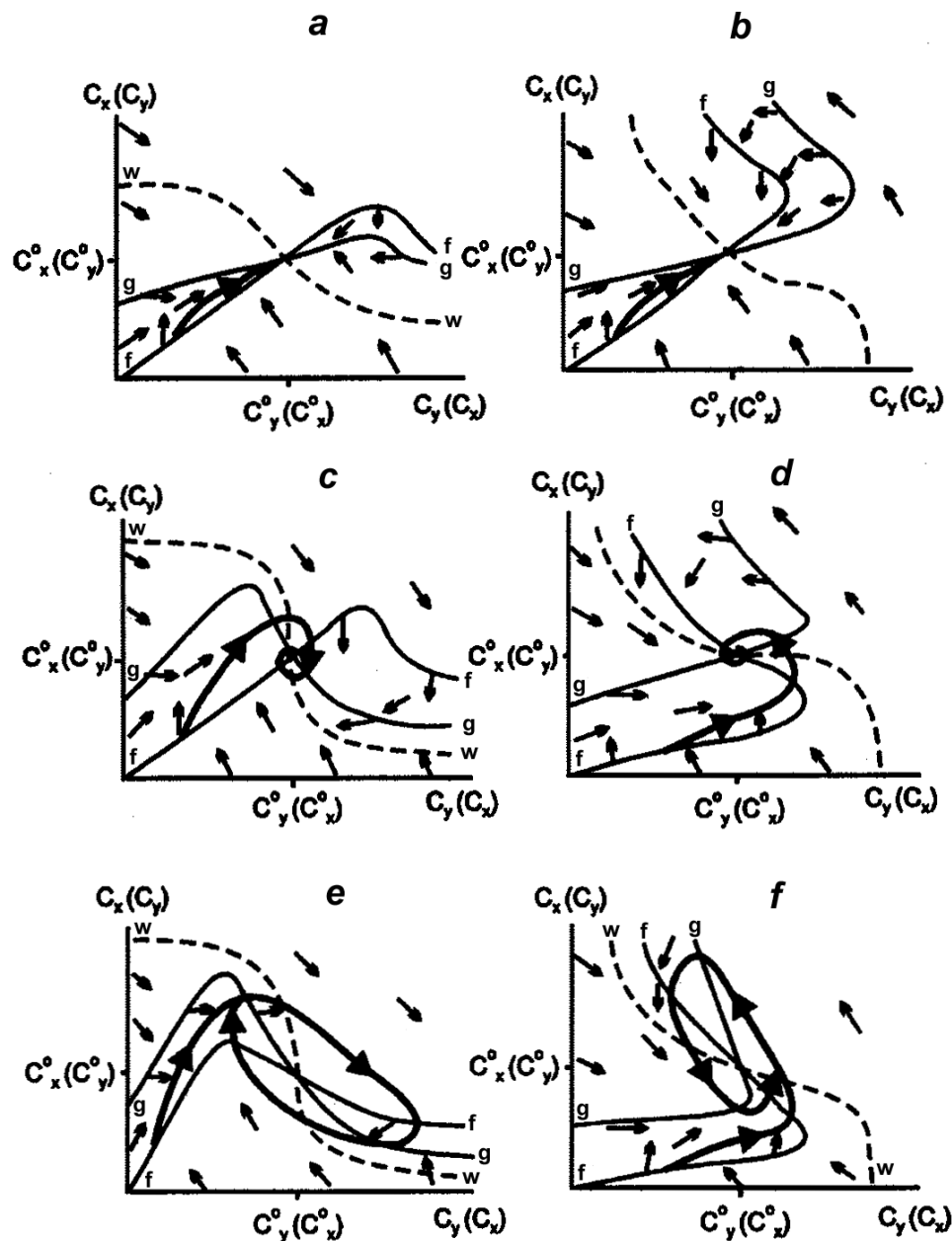


Fig. 4.12. Phase portraits of solutions of systems of equations of oscillating fronts and surface waves of phases (C_x, C_y) in dependence upon correlation of significant functions $f(F_{xy} = 0)$, $g(F_{xy} + wx = 0)$, $w(wx = 0)$.

F_{xy} is kinetics of oxydo-reducing reaction; w_x, w_y the kinetics of mass exchange reaction of the solution with solid phases of components x, y . Continuous bold lines are trajectories of solutions; arrows indicate their direction at a given point. C° is the component's solubility.

The phase portraits tally with various regions of dynamics of formation of metasomatic zones: *a, b* - regime of unidirectional zonality in conditions of local equilibrium in the zone (rest point, saddle point); *c, d* - regime of oscillating waves localized in rear limit of given metasomatic zone (stable and unstable focus); *e, f* - regime of oscillating waves disseminated everywhere in the given metasomatic zone (limited cycles around instable knot); *a, b, e* dextrogyre; *b, d, f* levogyre.

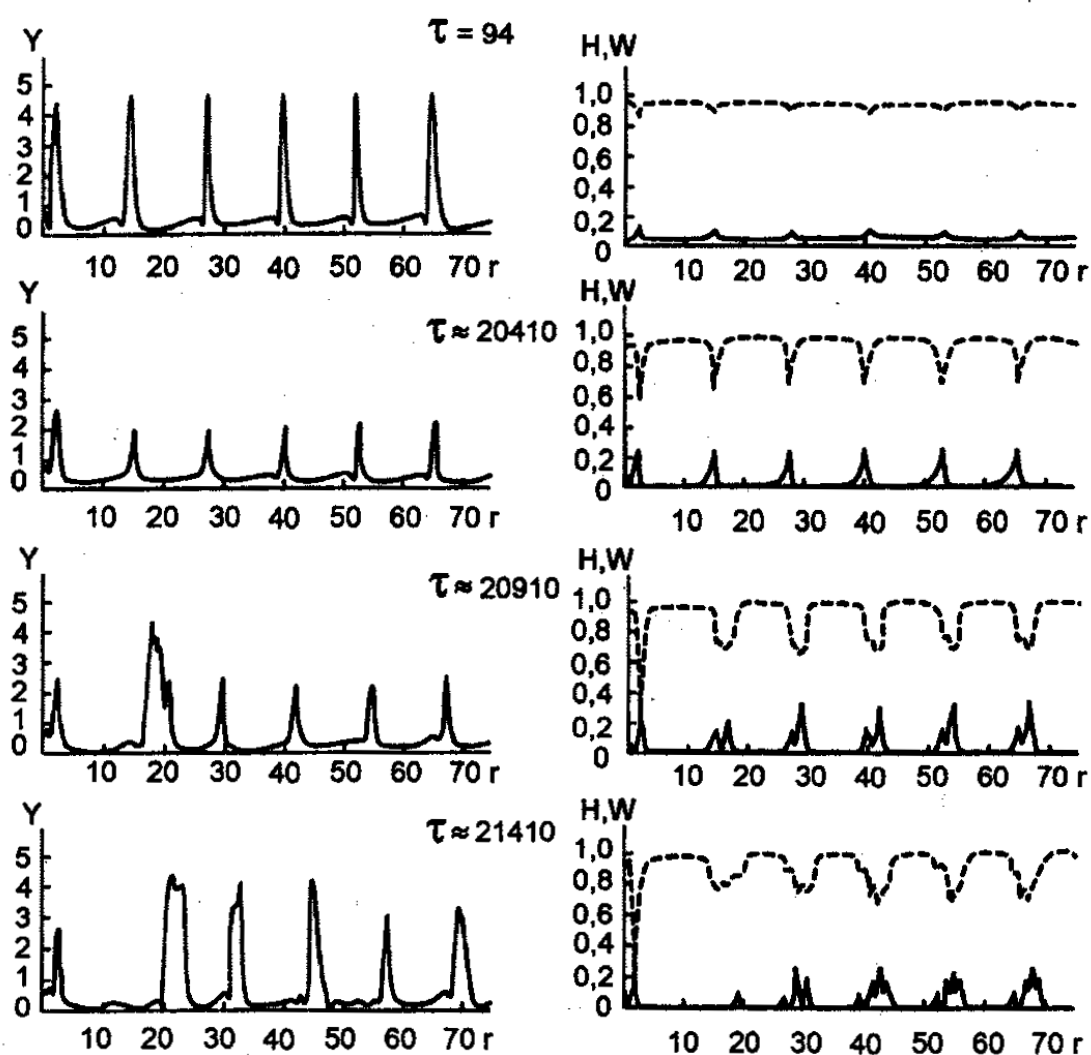


Fig. 4.13. Evolution of dissipative structure in solution (left) and evolution of the banded structure in rock (right) as result of computerized modelization .

Y is concentration of component in solution; H , W are contents of minerals in rock (H hedenbergite, W wollastonite), τ is extended time, r is distance in the direction of solution's filtration.

Chapter 5

Experimental modeling of metasomatism

In the course of the last decade experimental modeling has permitted to reproduce the main types of perimetalliferous metasomatic rocks and to appraise the border conditions of their formation depending upon T , P , P_{CO_2} , the solution's composition and concentration, pH , f_{O_2} and other parameters [Zaraisky, 1989, 1993^{1,2}; Zharikov & Zaraisky, 1991]. In the present work, the results of these researches have been used to interpret the physico – chemical conditions of metasomatic processes in granitic systems, between which are distinguished infiltration and diffusion (fig.5.1).

5.1. Experimental methodology

The basic volume of experiments was carried out by the method of modeling of diffusion metasomatic zoning. The method's main feature was D.S. Korzhinsky's modeling of an open system with perfectly mobile components. The latter's external activity in relation to the rock milieu was kept constant at the expense of the great buffer volume of the solution, in which was placed a small golden capsule open on one side ($d=5\text{mm}$, $l=50\text{mm}$) filled with compressed rock powder with grains smaller than or equal to 0.1 mm. As initial granitoidic rocks were used leucocratic granite, biotite granite and granodiorite (table1). The capsule with rock powder was placed vertically in a hermetic autoclave sheath of 150 cm³ prepared from an alloy of corrosion resisting titanium (fig.5.2). The sheath was filled with the solution and of necessity were introduced oxygen buffers and others, solid CO₂, weight gauged, pulverized quartz for the silicate solution's saturation, metallic and other components depending upon the experiments' conditions. The flow/rock relation stood about 100/1.

Table 5.1. Chemical (% weight) and mineral (% volume) compositions of granitic rocks utilized in experiments

	Rocks		
	Leucogranite ¹	Biotitic granite	Granodiorite ³
SiO ₂	76,87	71,06	65,56
TiO ₂	0,30	0,20	0,72
Al ₂ O ₃	12,56	14,59	15,52
Fe ₂ O ₃	0,38	0,30	-
FeO	-	1,75	3,64
MgO	0,10	1,20	2,19
CaO	0,50	1,74	3,98
Na ₂ O	3,80	4,14	3,76
K ₂ O	4,98	4,27	3,48
perte au feu	0,31	0,81	1,15
total	99,80	99,85	100,00

¹ – KazCentral Kazakhstan, Akchatau : Qtz-35,0 ; Pl-34,0 ; Kfs-29,0 ; Bi-1,0 ; etc.-0,1

² – Altaï (Kalbu), Belaïa Gora : Qtz-25,0 ; Pl-45,5 ; Kfs-19,0 ; Bi-9,5 , etc-1,0

³ – Tadjikistan, Maykhura : Qtz-23,5 ; Pl-45,5 ; Kfs-14,5 ; Bi-10,0 ; Amph-5,5 ; etc.-1,0

Use was made of solution of acids (HCl, HF), bases (NaOH, KOH) and salts of rock-forming components: chlorides and fluorides of Na, K, Ca, Mg, Fe as well as carbonates and metasilicates of Na and K in various combinations depending upon the task of modeling. In many experiments the solution's basis were NaCl or KCl as the prevalent components of natural fluids that acidified HCl or alkalified NaOH to obtain the indispensable amount of pH. Concentration of liquids varied in broad limits from 10⁻⁵ to 5moles/kg H₂O, but more often concentrations from 10⁻³ to 1.0m were adopted. In the course of the experiment the fluid remained motionless and reacted with the rock by the components' diffusion through the capsule's open orifice. In opposite direction occurred by diffusion the removal of the rock's components. Owing to the solution's great volume, its composition did not much vary in the course of the experiment, despite its reciprocal action with the granite. Granite got into equilibrium with the external solution only in the hindmost zone at the capsule's open end, More deeply the rock remained in unbalance with the external solution, but found itself, in each section, in a state near local equilibrium with its porous solution. To this was included, naturally, modeling of an open system with perfectly mobile components, whose activities, like pressure and temperature, were determined outside in relation with the kind of milieu. In experiments with fluorid solutions, instead of titanium sheaths smaller ones in gold or platinum were used and smaller capsules. The experiments were made at T = 250-600°C, P = 1 kbar and lasted one to four weeks.

At the end there appeared in the capsule, instead of the initial homogeneous rock, a zonal metasomatic column, frequently with sharp contact zones. The greatest change took place in the rear zone at the capsule's open end and in direct contact with the influencing solution. The first zone (towards the diffusion flow of the components) situated on the capsule's closed end remained in composition near the initial granite. The experimental columns were sealed with an organic glue and cut lengthways by means of a diamond saw and examined under the microprobe with the usual punctual method and the scanning method with a narrow beam along transverse profiles in order to determine the zones' global chemical composition.

We consider experimental models only of those main types of metasomatic rocks that form directly on granites, leaving aside another metasomatic main group genetically linked to granites but usually localized in intervening rocks (magnesium metasomatites of exocontact, propyllites, berezites, quartz-sericite, quartz-adular-sericite metasomatites and others). Taking into account the habitual close link of metasomatism with ore formation, experimental modelling was also carried out of deposits of rare minerals, synchronous with processes of acid and alkaline metasomatism of granite.

5.2. Modelling of acid metasomatism of granites.

The term acid metasomatism, or “acid leaching” [Korzhinsky, 1953], or “hydrogenised metasomatism” [Hemley & Jones, 1964], used as generic for a large group of metasomatic formations, is characterized by a common tendency to remove basic chemical components (Fe, Mg, Ca) and alkalines (K, Na) with increase of the rock's general acidity. Formation of rear zones only composed of siliceous and aluminous minerals or even only of quartz is the final result of the most intensive display of acid metasomatism.

Granite metasomatism under the action of acid chloridic solutions.

Modelling of formation of secondary quartzites. Under the influence on granite, granodiorite or quartz – diorite of aqueous solutions of HCl or chloruried acid solutions with weak ratio $m\text{KCl}/m\text{HCl}$, $m\text{NaCl}/m\text{HCl}$, $m\text{CaCl}_2/m\text{HCl}$, quartz saturated, metasomatic columns are formed, the rear zone of which is made up of quartz and of one of its alumino – silicated minerals: kaolinite (under 300°C), pyrophyllite (300-420°C) or andalousite (over 420°C) depending upon temperature [Zaraisky *et al.*, 1981]. As to mineral composition, these experimental metasomatites may be compared to facies of secondary quartzites with kaolinite, pyrophyllite and andalusite. They can be considered an extreme case of acid leaching of a granite, when in the influencing acid solution

any other rock-forming components, except silica, are absent (or present in tiny quantity).

Let us take as an example the structure of a metasomatic column obtained as a result of the influence on a biotite granite (cf. table 5.1) of a solution of 0.1M HCl for $T = 400^{\circ}\text{C}$ (fig. 5.3). The minerals' quantitative relations (%mol) in the column's zones were calculated on data of determination of the gross chemical composition with the microprobe scanning method with along a cross-section (table 5.2). For simplicity's sake we have not shown the part of porosity forming in the different zones from 28 to 41 vol.%. We note that in table 5.2. the porosities on hand refer to low values of the sum of chemical components, since by means of analysis with microprobe scanning the content of the component is determined in the smallest volume of porous environment. And only in the absence of pores does the sum reach 100%. The data on table 5.2 show that in the process of metasomatism FeO, MgO, CaO, Na₂O and K₂O undergo an important removal, but that the content of SiO₂, Al₂O₃ and TiO₂ remains exactly at the previous level, albeit silica always shows some leaching in rear zones 1 and 2.

Table 5.2. Chemical composition (% weight) of the metasomatic zones of the experimental column, corresponding to the quartz –pyrophyllite facies of secondary quartzites (cf. Fig. 5.3)

	Zone					
	1	2	3	4	5	0 ¹
SiO ₂	48,4	45,7	49,9	53,2	50,7	49,7
TiO ₂	0,2	0,2	0,4	0,3	0,3	0,2
Al ₂ O ₃	10,6	10,6	10,2	10,2	10,1	10,2
FeO*	0,1	0,6	2,3	1,4	1,3	1,4
MgO	0,0	0,0	1,0	0,7	0,7	0,9
CaO	0,1	0,3	1,0	1,0	0,9	1,2
Na ₂ O	0,2	0,3	1,4	2,6	2,5	2,9
K ₂ O	0,2	1,5	2,7	2,9	3,3	3,0
Somme	59,8	59,2	68,9	72,3	69,8	69,3

* All iron as FeO

¹ 0 – initial biotite granite, porosity=30 %

Temperature decrease to 300°C or less brings about formation, in the rear zone, of kaolinite instead of pyrophyllite, whereas in the experiments at 500°C andalusite is formed instead of pyrophyllite. Everywhere in the rear zones, quartz is present as second phase. At all temperatures in the column's central zones muscovite develops. The succession of replacements, feldspar → muscovite → pyrophyllite (kaolinite, andalusite) reflects the solution's acidity increase through movement in the column from fore zones towards rear

zones. The succession of replacements with temperature, in the rear zones of the column of kaolinite by pyrophyllite and andalusite tallies with the change of temperature facies of secondary quartzes.

Modeling of quartz–muscovite greisens and quartz–potassic feldspar metasomatites.

With increase of the ratio $mKCl / mHCl$ in the active solution the granite's acid leaching decreases in intensity and in the rear zones of the columns appear the micas, feldspars and other alumino-silicates (fig.5.4).

Experimental columns formed in these conditions may be compared with the quartz – muscovite greisens and the quartz – feldspar metasomatites. So for example, due to the influence on a biotite granite of the solution $1\text{ mKCl} + 0.05\text{ mHCl} + (\text{quartz})$, $pH_{init}=1.4$, $T=400^{\circ}\text{C}$, $P=1\text{ kb}$, $t=500\text{ h}$, a column has been obtained that approaches in composition and succession of zones the greisens of quartz – muscovite facies (figures below indicate distance of zone limits from the capsule's open end).

Ms+Q tz	Ms+Qtz+K fs	Ms+Qtz+Kfs +Bi	Ms+Qtz+Kfs+Pl +Bi	Qtz+Kfs+Pl+ Bi	Bi-granit
0	2.8	6.1	33.7	43.7	48.7 mm

In similar experiments, but without quartz saturation of the column, the rear zone is only composed of muscovite with strong porosity. Such columns may be compared with the greisens of muscovite facies and of quartz – muscovite, rarely present in nature.

Due to influence on a biotite granite of a strongly acid but highly potassium – concentrated solution $3\text{mKCl}+0.1\text{mHCl}+[\text{quartz}]$, $pH=0.8$ for $T=500^{\circ}\text{C}$, $P=1\text{ kb}$, $t=240\text{ h}$ a metasomatism column with quartz-potassic feldspar has been reproduced, in which granite was replaced at great depth by a quartz – potassic feldspar aggregate:

Qtz+Kfs	Qtz+Kfs+B i	Biotite granite
0	35.0	50.0 mm

And in this case the influence of solutions undersaturated in quartz produces a monomineral rear zone of potassic feldspar.

At a temperature higher than 450°C quartz – muscovite greisens are replaced, with increase of acidity (decrease of the ratio $mKCl/mHCl$), by the quartz – andalusite facies of secondary quartzites or greisens, but under 300°C by a quartz – kaolinite facies.

Conditions at the limits of formation of secondary quartzites, quartz – muscovite greisens and quartz – potassic feldspar metasomatites for a temperature and value of the equilibrium ratio $mKCl/mHCl$ in the solution may be represented on the experimental diagram of phase relations in the granitic system model $Al_2O_3-SiO_2-H_2O-KCl-HCl$ (fig. 5.5).

This system tallies with the composition of the most modified rear zones of the acid metasomatic columns, from which are removed all rock-forming components, except Si, Al and K. Therefore the phase composition of the diagram's field tallies with the mineralogical composition of the rear zone columns of corresponding metasomatic formations and facies. The upper temperature limit of quartz – muscovite greisens is determined by thinning out of the stability field of muscovite in association with quartz at 555°C. With a PH_2O increase it rises a little (up to 590°C at 2 kbar), but with a decrease it sinks (to 500°C at 0,5 kbar). Quartz feldspar metasomatites may exist in a very wide range of temperature in conditions of increased potassic solutions. This being so, with temperature decrease at constant HCl concentration it is necessary to have the highest KCl concentration for an exchange of quartz – muscovite and quartz – feldspar mineral association.

Modelling of quartz – albite metasomatism and propylitization of granitoidic rocks. Under the influence of sodic solutions, albitization stands as the leading process of granite change. However, very acid Na containing solutions of the type $1mNaCl + 0.1mHCl + [quartz]$ exert on granite nearly the same influence as solutions of one HCl, i.e. bring about formation in rear zones of columns of Qtz+Kln, Qtz+Prl or Qtz + And associations. Such columns tally with the different facies of secondary quartzite formation. The cause of this is neither presence nor absence of sodium in the solution, but high acidity. Under influence of moderately acid, nearly neutral chloridic solutions with a different sodium concentration (from 0.01 m to 5m NaCl) on a leucocratic granite (cf. table 5.1), all the minerals of the initial rock, except quartz, are albitized, there forms a metasomatic column of quartz albite type ((T=400°C, P=1kb, t=336 h, solution 1m NaCl+[quartz], $pH_{init}=5.8$):

Ab+Qtz	Ab+Qtz+Bi	Ab+Qtz+Kfs+Bi	Leucogranite
0	6.0	15.0	50.0 mm

Kfs at first, then biotite are replaced by albite. Relicts of initial oligoclase are sometimes preserved. The rear zone is composed only of albite and quartz. A certain increase in the solution's acidity brings about muscovite in the transition zones of the column in paragenesis with biotite, albite and quartz.

Influence of near neutral and weakly sodic solutions on granodiorite (cf. table 5.1) at T=300-500°C produces formation of column of the type albite propylites, the rear zone of which is made up of paragenesis of AB + Chl +

Amph + Zo (the solution SiO_2 — undersaturated). For $T=500^\circ\text{C}$, $P=1\text{kb}$, $t=336\text{ h}$, solution $1\text{m NaCl} + 0.0003\text{m HCl}$, $\text{pH}_{\text{init}}=3.7$, we get the column:

Ab + Amph + Chl + Zo	Qtz + Ab + Amph + Chm + Zo	Qtz + Pl + Amph + Bi + Chl + Zo	Ganodiorite
0	2.0	4.5	21.0
			50 mm

As acidity increases from the composition of quadrimineral paragenesis of the rear zone, successively disappear amphibole, zoisite and albite. Much more stable is chlorite, which associates with paragonite in moderately acid sodic solutions. In conditions of high acidity chlorite disappears, the column's rear zone is made up of Kln, Prl or And, to which quartz is added at the solution's silica saturation.

Metasomatism under the action of acid fluoridic solutions.

Modeling of granite's greisenisation. Participation of acid fluoridic solutions is the most characteristic of greisen formation processes, in particular of formation of quartzous and quartz – topaz greisens with fluorite and F-containing micas. By Io.B. Shapovalov [Shapovalov, 1988] were obtained the first experimental data on topaz's mineral equilibrium in the system $\text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O} - \text{KF} - \text{HF}$ (fig. 5.6).

It is established that topaz's formation requires high enough concentrations of HF and low KF in a solution in equilibrium ($\text{mHF} > 0.0025\text{m}$, $\text{mKF} < 0.006\text{m}$ pour $T=400^\circ\text{C}$, $P=1\text{kb}$). This accounts for the limited expansion of topaz greisens in nature. Depending on temperature the topaz's low stability limit is determined by equilibrium with andalousite, pyrophyllite or kaolinite. The upper limit at all studied temperatures ($300\text{-}600^\circ\text{C}$) is defined by equilibrium with fluellite ($\text{AlF}_3 \cdot \text{H}_2\text{O}$).

Greisens of quartz – topaz facies. The acid fluorid solution's peculiarity consists in the great solubility in them not only of silica but also of aluminium [Zaraisky, 1999]. That is why to prevent granite dissolving in experiments with a solution HF, crushed quartz and corundum have been added. Thus we succeeded in obtaining for leucocratic granite (cf. table 5.1) a zoned column tallying with the greisens' quartz – topaz facies ($T=500^\circ\text{C}$, $P=1\text{kb}$, $t=336\text{ h}$, solution $1\text{mHF} + [\text{quartz}] + [\text{Al}_2\text{O}_3]$):

Qtz + Toz + Fl	Qtz + Ms + Fl	Qtz + Ms + Kfs + Fl + (Ab)	Qtz + Kfs + Ab + Fl	Qtz + Ab + Kfs + Bi + Fl	Leucogranit e
0	3.0	4.1	7.2	2.1	25 mm

Quartz in rear zone predominates over topaz (fig.5.7). In the following zones topaz is replaced by muscovite, even more deeply, stability of potassic feldspar is retained and also, later on, that of albite of the initial leucocratic granite. In all zones fluorite is present up to 1 to 3%.

Greisens of quartz-muscovite of facies. A weak increase of potassium concentration in the solution ($mKF > 0.006m$) leads to replacement of topaz in the rear zone by muscovite and increase in the quantity of potassic feldspar in the remaining zones:

Qtz + Ms + Fl	Qtz + Kfs + Ms + Fl	Qtz + Kfs + Ms + Bi + Fl	Qtz + Kfs + Ab + Bi + Fl	Leucogranite
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Greisens in quartz facies. In chlorured solutions we did not succeed in obtaining a column corresponding to quartz greisens, due to preservation of alumine in the rear zone. However, alumina can be completely eliminated from the rear zone due to reciprocal action of leucogranite with the quartz saturated solution HF. In an experiment performed at $T=900^{\circ}C$, $P=1kb$, $t=336$ h, the solution $1mHF + [quartz]$ in excess produced a column with a practically monoquartzic rear zone:

Qtz + Fl	Qtz + Ms + Fl	Qtz + Kfs + Ms + Fl	Qtz + Kfs + Ab + Bi + Fl	Leucogranit e
0	3.0	5.0	7.5	25 mm

To form the most complete column with a different quartz-topaz zone between quartzic and quartz-muscovite zones a higher alumina activity is needed in the solution ($T=500^{\circ}C$ $P=1kbar$, $t=336h$, solution $1m HF+0,17m AlF_3+[Qtz]$):

Such a lateral zoning is namely characteristic of symmetrically zoned subvertical veined greisens bodies in the wolfram-molybdeniferous deposits of Akchatau in Central Kazakhstan [Zaraisky 1995].

The results of experimental modelling confirm the need of participation of acid fluorid solutions in greisens forming processes. In fact, under influence of fluorid solutions all types of fundamental facies of greisens can be obtained: quartz-muscovite, muscovite, quartz-topaz and quartz, whereas chlorid solutions can only bring about formation of quartz-muscovite and muscovite facies. The example of greisens allows us to speak of secondary role of temperature as compared with the solution's composition. All types of greisen columns characterized above were obtained in a wide range of temperature, from 300 to $600^{\circ}C$ [Soboleva & al. 1988] and then the columns' structure varied very

weakly with the temperature change, and it decidedly depended upon the variation in the solution' composition.

Metasomatism under the action of chlorinated and boric acid solutions.

In H_3BO_3 solutions without other components added, tourmalinisation has not been reproduced. By adding NaCl tourmaline is formed only in the rear zone of the metasomatic column on account of the dark-hued minerals of the rock. By adding FeCl_2 , FeCl_3 or MgCl_2 tourmaline formation is much intensified in all the column's zones on account of dark-hued minerals as well as of feldpars. In conditions of acid increase ($\text{pH} = 1.5$ to 4.0) it is necessary, in order to obtain quartz-tourmaline greisens and other metasomatites with tourmaline, to have a high concentration of H_3BO_3 , from 0.5m at 600°C to 2.0m at 300°C . It is established that tourmaline is always less ferriferous compared to the equilibrated ferruginous solution and it shows a tendency for its ferruginosity to increase as temperature decreases.

Metasomatism under the influence of chlorinated solutions containing CO_2 and sulfur.

The fundamental part of this series of experiments were carried out at a moderately low temperature, from 250 to 400°C . In dependence on stability of clayey minerals, sericite and potassic feldspar in the rear zone, the experimental columns may be confronted with three groups of metasomatites: 1) argillisites, 2) beresites and metasomatites with quartz-sericite, 3) gumbeites and metasomatites with quartz-potassic feldspar. Typomorphic minerals of beresites, gumbeites and argillisites, except fixed aluminosilicates, are ankerite, calcite and pyrite. On the diagrams in the coordinates $T\text{-}P\text{-}X\text{CO}_2\text{-}\log(\text{mK}^+/\text{mH}^+)$ the field of beresites occupies a central position (fig.5.8). With decrease of temperature and value of ratio $\log(\text{mK}^+/\text{mH}^+)$, beresites are replaced by argillisites, but with increase of those parameters, by gumbeites. Pressure variation acts in the opposite direction. Remarkable is the rather narrow temperature range of beresite formation (optimum T : $260 - 325^\circ\text{C}$) and their strong dependence upon CO_2 concentration in the fluid ($X\text{CO}_2 \geq 0.05$). Decrease of $X\text{CO}_2$ brings about replacement of beresites by quartz-sericite metasomatites containing no ankerite carbonate. Analogous correlations occur between ankerite-containing gumbeites and quartz-potassic feldspar metasomatites without ankerites.

5.3. Modeling of alkaline metasomatism of granites

Metasomatism of carbonates and silicates of sodium and potassium under the action of chloride solutions

Modeling of aegyrine albites and potassic feldpars. In conditions of sodic alkaline metasomatism for an excess of quartz there is only an intense removal of K_2O from the granite and significant addition of Na_2O [Zaraisky, 1989]. Feldspars are replaced by albite and biotite by aegyrine. As final result of the change is found a rear zone of quartz-albite- aegyrine. (T=500°C, P=1kb, t=336 h, solution 1.0mNaCl+1mNaOH+[quartz], pH_{init}=12.8):

1	2	3	0
Qtz + Ab + Acm	Qtz + Ab + Acm + (Bi)	Qtz + Pl + Kfs + Acm + (Bi)	Granite in biotite
0	8.2	27.7	44.5 mm

On table 5.3 has been adduced the chemical composition of zones of this column which it is interesting to compare with that of zones of acid leaching columns (cf. table 2). Through acid leaching of the granite's biotite, including in acid solutions with high Na activity, an intense removal of all components occurs from the rock, except alumina but including some removal of Na. In the alkaline sodic metasomatism, from the granite, K_2O is strongly leached (partly also MgO) and much Na_2O is added. The granite's alumina concentrates in albite, and through addition of Mg, Ca and Ti to the granite aegyrine is formed.

The action of sodic alkaline SiO_2 undersaturated solutions brings about the granite's strong desilicization. Instead of albite associated with aegirine are formed in the rear zone feldspathoids, nepheline, sodalite or cancrinite depending on the anionic composition of the solution (OH^- , Cl^- or CO_3^{2-}). Evidently the condition of such high alkalinity is not typical of granitic massifs.

Potassic alkaline solutions bring about the granite's potassic metasomatism, expressed in intense potassic feldspathisation. The rear zone has the mineral composition Qtz + Kfs + Bi. In the SiO_2 undersaturated solutions, the rear zone is made up of potassic feldspars. By very high alkalinity (solution 1.0m KOH) in the rear zone is formed, instead of Kfs, calcite associated with tetraferribiotite. In the middle and forward zones of such columns calcite is replaced by potassic feldspar, and on the biotite are formed aegyrine and riebeckite.

Table 5.3. Chemical composition (% weight) of the metasomatic zones of the experimental column, of alkaline, sodic metasomatism of biotite granite (column of aegiritic albitites)

	Zone			
	1	2	3	0 ¹
SiO ₂	49,7	49,9	51,8	49,7
TiO ₂	0,2	0,2	0,3	0,3
Al ₂ O ₃	9,3	9,5	9,7	10,2
FeO*	1,2	1,1	1,5	1,4
MgO	0,5	0,3	0,5	0,9
CaO	1,0	1,1	1,2	1,1
Na ₂ O	6,0	4,6	3,8	2,9
K ₂ O	0,2	0,7	2,4	3,0
Total	68,1	67,4	71,2	69,5

* All iron as FeO

¹ 0 – initial biotite granite, porosity = 30 %

Metasomatism under the action of alkaline fluorid solutions

Modeling of alkaline albitites and “apogranites” with riebeckites and aegyrines.

Presence of fluorite, cryolite, F-containing amphiboles and micas is usual in many alkaline metasomatites developing in normal and alkaline granite. One of the interesting problems is the possibility of formation of metasomatism of granite with riebeckite and aegyrine, in the way of what we considered above [Zaraisky & Zerianov, 1973].

In alkaline fluorid solutions the most intense granite transformation occurs in absence of quartz saturation (T=500°C, P=1kb, t=95 h, solution 1.0 mNaF, pH_{out}=7.2):

Ab + Rbk	Qtz + Ab + Rbk	Qtz + Ab + Ksp + Rbk + (Bi)	Biotitic granite
0	1.0	12.0	40.0 mm

In the column's rear zone is formed riebeckite albitite: quartz is eliminated, potassic feldspar and plagioclase are completely albitized, but biotite is replaced with alkaline amphibole. Meanwhile the column's transition zone tallies in composition with the typical riebeckitic granite. Temperature increases up to 500 or 600°C brings about replacement of riebeckite by aegyrine.

When the fluorid-sodic solutions are silica saturated, granite transformation diminishes, quartz is preserved in the rear zone, while potassic feldspar remains more stable. Increase of SiO_2 activity furthers aegyrine development instead of alkaline amphibole. However, the column's transition zone tallies even then with the ribekitic granite. This same paragenesis, of typical riebeckite granites (Qtz + Ab + Kfs + Rbk) occurs in the transition zone even under the influence upon biotitic granite of potassic alkaline fluorid solutions instead of sodic ones ($T=500^\circ\text{C}$, $P=1\text{kb}$, $t=96\text{h}$, solution 1.0m KF, $\text{pH}_{\text{init}}=7.3$).

Kfs + Fe-Bi	Kfs + Nar	Qtz + Kfs + Rbk	Qtz + Ab + Kfs + Rbk + (Bi)	Bi-granite
0	1.5	14.0	35.0	40.0 mm

In this, buffering action of the rock is manifested, supplying Na to the porous solution at the albite's replacement by potassic feldspar. However, depending upon the external solution's cationic composition, the column's rear zone consists either of albite and riebeckite (NaF solution) or of potassic feldspar and tetraferri-biotite (KF solution). So is notably formed narsarsukite, $\text{Na}_2(\text{Ti,Fe})\text{Si}_4\text{O}_{10}(\text{O,OH,F})$, in the column's second zone, obtained in the KF solution.

5.4. Dependence of facies of alkaline sodic metasomatism of granitoidic rocks upon temperature and values of $\log(m\text{NaCl}/m\text{NaOH})$ in the solution

In this series of experiments the initial rock was granodorite (cf. table 5.1) and 1.0m NaCl was the solution's basis. A change in alkalinity was obtained by increasing NaOH from 0.0001 to 0.1m. The initial pH value increased from 7 to 12.8. The solutions were silica-undersaturated [Zaraisky *et al.*, 1984].

As the solution's alkalinity increased, the type of arising metasomatites changed from albite propyllites in near neutrality to alkaline amphibole-aegyrine-albitites and ultra-alkaline aegyrine-riebeckite-sodalite metasomatism (fig. 5.9).

With temperature decrease from 400 to 350-300°C sodalite and albite are replaced by analcime. An important limit between the fields of acid and alkaline metasomatism is fixed by the replacement of actinolite amphibole in the propyllites by alkaline amphibole in the albitites. In the P-T conditions of the experiments this limit runs parallel to the line of neutral values of the $\text{pH}_{\text{T,P}}$, somewhat altered in the alkaline field. Analysis of solutions after experiments reveals a sharp decrease (a hundred times) of removal from the rock of Fe, Mg and Ca in alkaline, compared to acid conditions.

5.5. Modelling of deposits of rare metals (W, Mo, Sn) in the process of greisenisation and alkaline metasomatism of leucocratic granite

In this series of experiments were used as source of W, Sn and Mo swallowed wolframite, molybdenite and cassiterite crushed in a solution in a separate bowl [Zaraisky & Stoyanovskaya, 1995]. As in other experiments, condensed leucogranite powder was placed in an open golden capsule. Owing to reciprocal action with the solution there appeared on the granite a metasomatic column of diffusion with added quantities of W, Mo and Sn in the rear zones. As means of “greisenizing” were utilized acid chlorured and fluorured solutions: 1m KCl + 0.5m HCl and 1m KF + 0.05m HF. For comparison's sake we have studied the influence of a nearly neutral solution of 1m NaCl, producing leucogranite albitization, and of two alkaline solutions of 0.1m Na₂SiO₃ and 0.1m Na₂SiF₆, producing alkaline albitites on the granite. The obtained metasomatic columns were cut up lengthwise and studied with microprobe, but also, analysed, for ore components, by the method of quantitative spectral layer-by-layer analysis, for which 6 or 7 trials were carried out on each line of the column.

It was established that W, Mo and Sn may be transported in sufficient quantities by solutions of varied composition, producing the granite's greisenization, albitization and alkaline metasomatism and be deposited synchronously with the formation of these metasomatites, mainly in the rear zones of the metasomatic columns (fig. 5.10). Instead of which, the mentioned elements show an appreciable difference in their migratory capacity, to which may be linked their frequent zonal distribution in the deposits.

We discover the marked dependence of rare metals' addition and precipitation upon the solution's composition and acido-alkalinity (fig.5.11). So, for example, W, Mo, and Sn are equally well transported by alkaline solutions. At the same time, acid chlorured solutions are rather favourable to wolfram transport and precipitation, but less so to molybdene transport. Tin migrates farthest in solutions of Na₂SiF₆ and NaCl. Moderately acid fluorid solutions worse than others deposit W and more easily Sn and Mo. Wolfram is best introduced by very acid and very alkaline solutions and appreciably worse by nearly neutral solutions. Molybdene is deposited in columns in much smaller quantities than wolfram and tin and displays an inverse relation to the solution's acidity, showing the greatest accumulation in alkaline conditions. As a whole, at a lower level of accumulation in the metasomatic zones and the distance of migration to the column, the metals dispose themselves in the order W > Sn > Mo. Thus, tin is most indifferent to the solution's composition, but W and Mo show a more pronounced selectivity.

5.6. Conclusion

The most intense metasomatic changes of granites usually coincide with the peripheric intrusion zone, whereas in the granite's internal core the changes are usually weak and metalliferous mineralizations, as a rule, absent. Notably, the peripheric and especially apical part of an intrusion is characterized by the presence of local permeable structures (cracks, breach zones, compressed cupolas, apophyses) provoking fluid flows. This phenomenon has a general character and may be interpreted as the development in the intrusion's contact part of destructive thermoelastic tensions, conditioned by an irregular temperature distribution during the granitic body's crystallization and cooling down. In the internal part of the intrusion, thermo-elastic tensions do not reach destructive force, and cracks of thermal gradient are absent. Flow concentration in local fluid conductors brings about formation in the lateral rocks, in contrast, a marked diffusion of metasomatic zoning.

The type of metasomatic process depends on a combination of many physico-chemical parameters and finds its most complete expression in a zonal metasomatic column, a series of successive zones from unchanged granite to the final product of its change. The method of experimental modelling produces various types of metasomatic columns, nearly tallying with all natural metasomatites (metasomatic formations) developed in granites.

For the formation of such and such a type of metasomatic column, most significant is the composition of the rock and of the solution and its pH. Temperature, pressure and other parameters are less important. So, for example, for the formation of topaz greisens, action of acid fluorid solutions on the granite is indispensable ($>10^{-3}\text{m HF}$ for 400°C and $>10^{-2}\text{m HF}$ for 500°C) with high alumina concentration ($>5 \cdot 10^{-4}\text{m } \Sigma\text{Al}$) and a low potassium activity ($<10^{-2}\text{m KF}$). Albite propylites determine the border field between acid and alkaline metasomatism; they are formed in nearly neutral conditions. For the formation of alkaline albitites with riebeckite-aegyrine, favourable are temperatures between $350\text{--}450^{\circ}\text{C}$ and the action of essentially sodic alkaline solution with $\text{pH} > 6.6$ to 8.5 . Under the action on granite of chlorured solutions in conditions of highest acidity (with low mKCl/mHCl ratio) arise metasomatic columns tallying with secondary quartzites. Successive increase of the mKCl/mHCl ratio at once brings about formation of columns of the quartz-muscovite greisens type or quartz-sericite metasomatites, and afterwards of quartz-potassic feldspar metasomatites (fig. 5.6). Many minerals of granitic metasomatites (quartz, potassic feldspars, muscovite, albite, topaz, tourmaline, epidote, riebeckite, aegyrine and others) are formed in a wide range of P-T conditions and cannot serve as indicators of the metasomatism's temperature or pressure, albeit their presence allows us to judge the solution's composition. The role of temperature is determining in the replacement of quartz-kaolinite facies of secondary

quartzite by quartz-pyrophyllite and quartz-andalousite facies. Presence of kaolinite in metasomatites indicate a temperature of the process not higher than 270-300°C, but of andalousite or coryndum, higher than 400°C. Pyrophyllite is stable between 300 and 400°C. Corundum and diaspore are incompatible with quartz and indicate undersaturated silica solutions.

Experimentally demonstrated is the possibility of ore deposits immediately in the process of acid and basic metasomatism of granite. For example W, Mo and Sn show a different migration capacity of metals and its precise dependence upon composition and acidity of the corresponding hydrothermal solution.

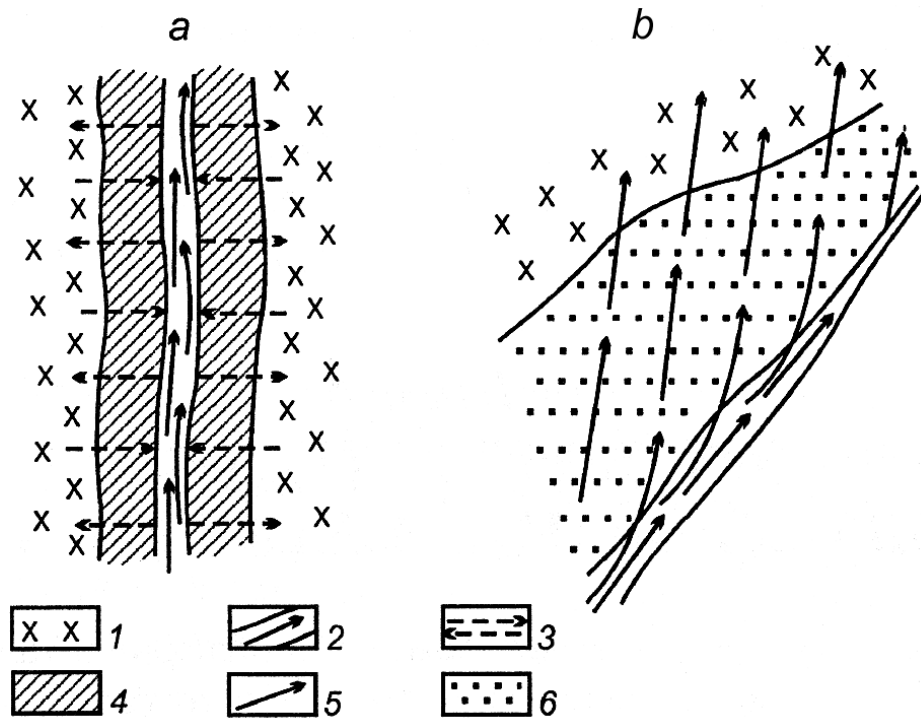


Fig. 5.1. Principal schemes of metasomatism manifestation in nature.

a – diffusion metasomatism; *b* – infiltration metasomatism; 1 - unaltered granite; 2 - infiltration flow of fluids along a fracture or in zone of high permeability in granite; 3 - diffusion flows of components in immobile pore solutions; 4 - symmetrical halo of diffusion metasomatic wall-rock alteration; 5 - infiltration flow of solution through thickness of granite; 6 - halo of infiltration metasomatic alterations in granite.

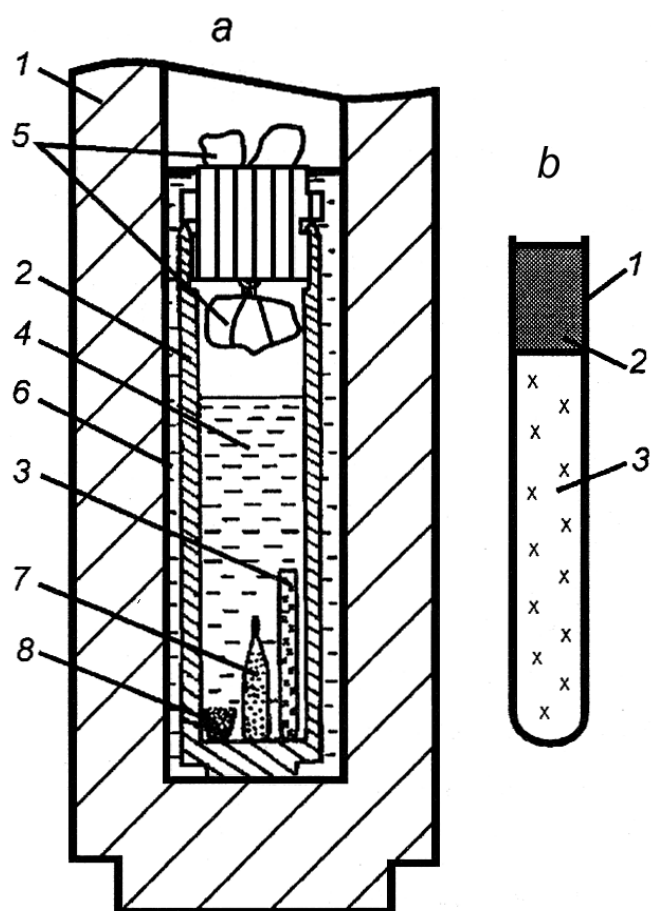


Fig. 5.2. Scheme of experiment on modelisation of diffusive metasomatism.

a - loading of the autoclave before experiment: 1 - capping of the autoclave, 2 - hermetic insert in titanium alloy, 3 - open gold capsule with granite powder filling, 4 - solution, 5 - solid CO_2 , 6 - distilled water, 7 - capsule with oxygen buffer, 8 - open platinum cup with powdered quartz, ore minerals or other solid substances.

b - capsule with granite after experiment: 1 - wall of the capsule, 2 - unaltered granite, 3 - column of diffusion metasomatic zones at closed end of capsule.

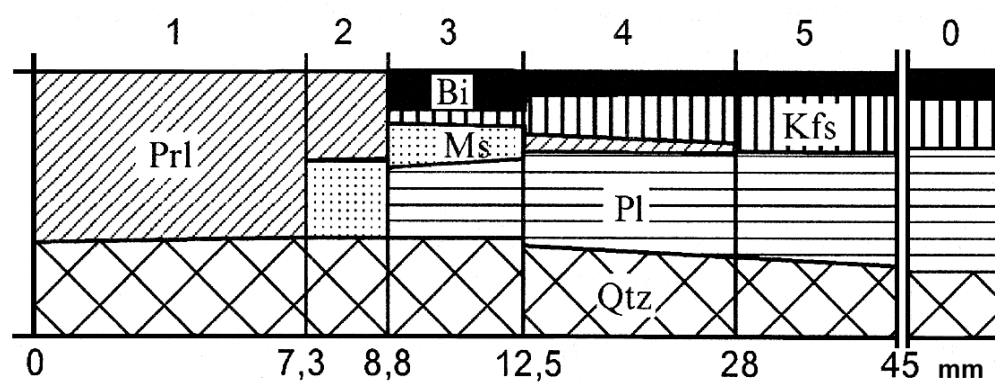


Fig. 5.3. Zonal pattern of experimental metasomatic column of acid metasomatism in biotite granite, corresponding to the quartz-pyrophyllite facies of secondary quartzites ($T = 400^{\circ}\text{C}$, $P = 1\text{kb}$, $t = 500\text{h.}$, solution $0,1\text{m}_{\text{HCl}} + [\text{Qtz}]$, $\text{pH}_{\text{max}} = 1,2$).

Global chemical composition of zones, see Table 5.2.

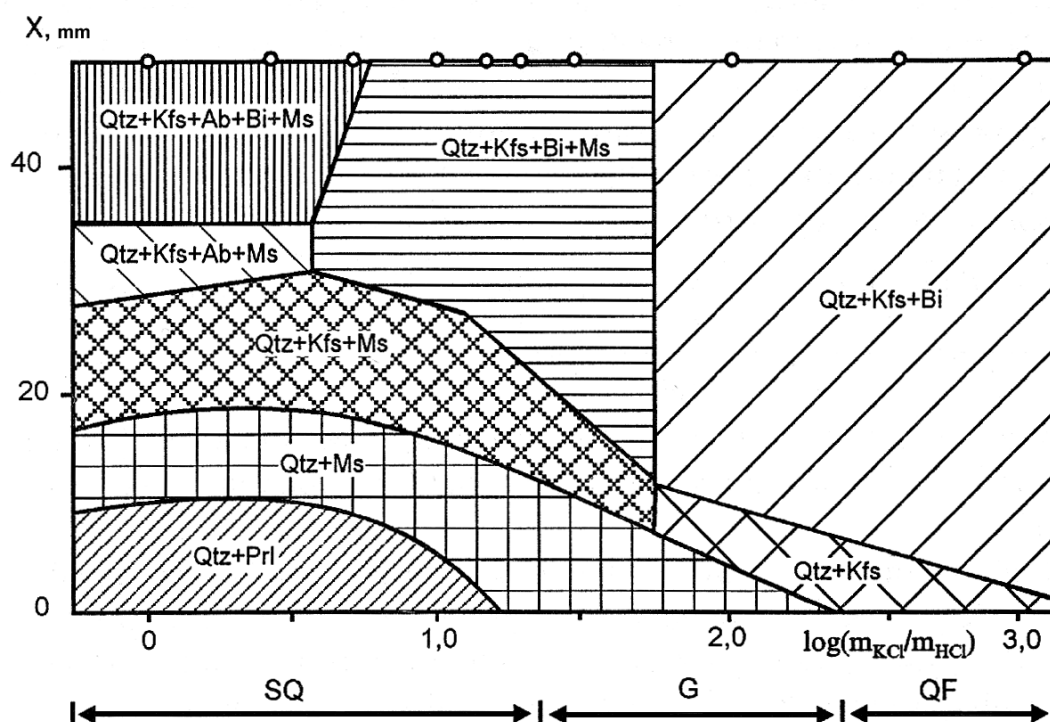


Fig. 5.4. Variations of zoning of experimental columns of acid metasomatism of a leucogranite in relation with values of ratio $\log (m_{\text{KCl}}/m_{\text{HCl}})$ in the solution ($T = 400^{\circ}\text{C}$, $P = 1 \text{ Kbar}$, $t = 336\text{h}$.)

SQ – secondary quartzites; G – greisens of quartz-muscovite facies ; QF – quartz-feldspar metasomatites.

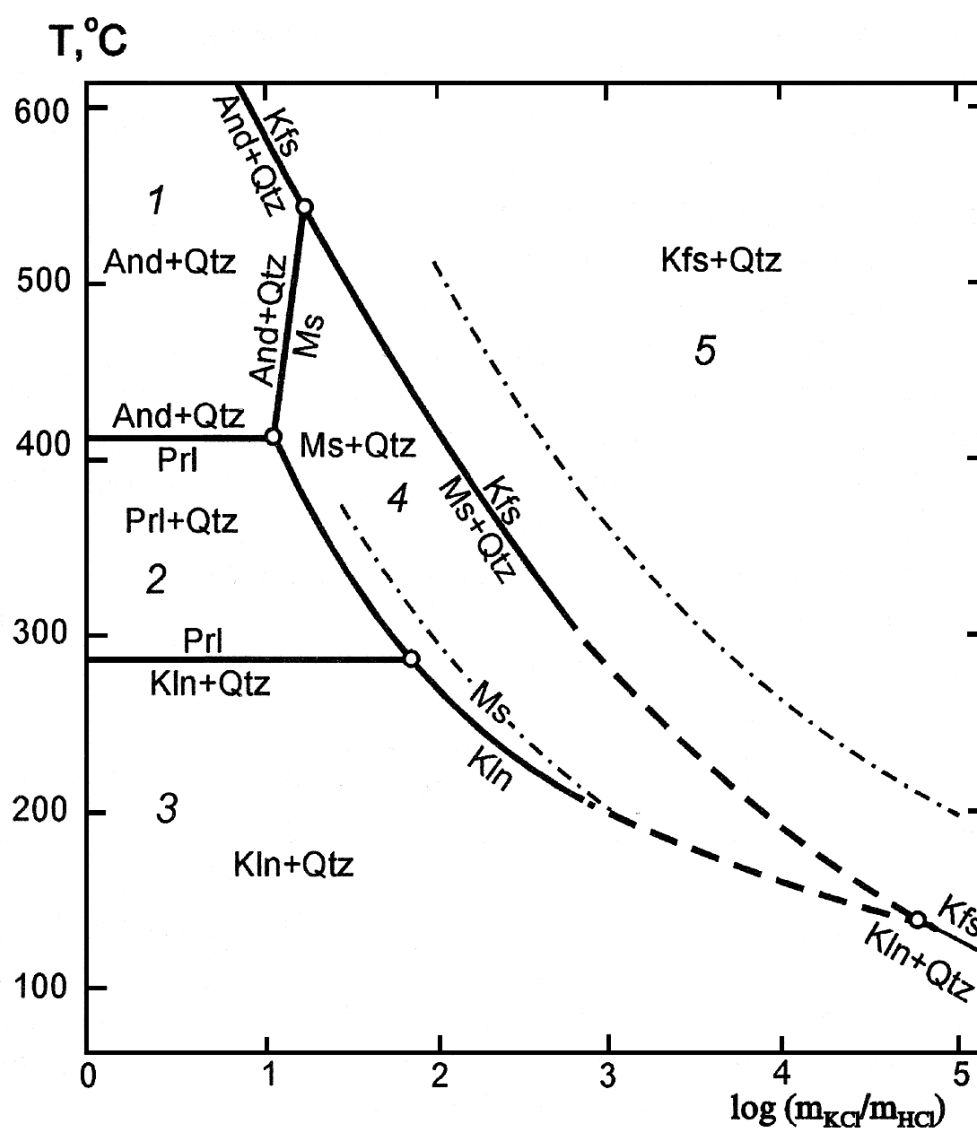


Fig. 5.5. Phase relations in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-KCl-HCl}$ for $P = 1 \text{ kbar}$ and excess of quartz [Zaraisky et al., 1981].

Digits indicate fields to which correspond in mineralogical composition inner zones of the column of metasomatic facies: 1, 2 and 3 quartz-andalusite, quartz-pyrophyllite and quartz-kaolinite facies of secondary quartzites correspondingly; 4 quartz-muscovite facies of greisens and quartz-sericite facies of secondary quartzites; 5 quartz-Kfeldspar metasomatites.

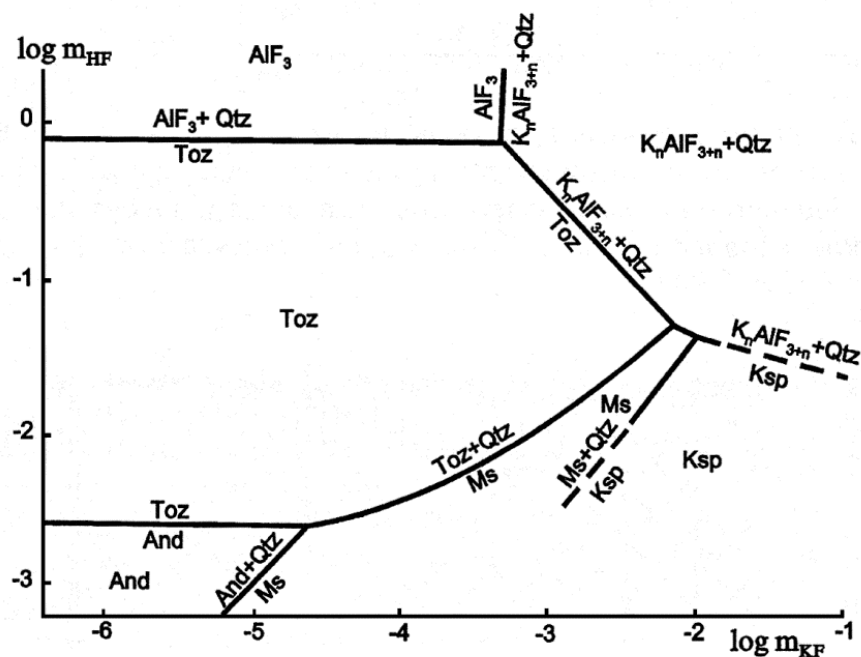


Fig. 5.6. Fields of stability of topaz and other minerals in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-KF-HF}$ in diagram $\log m_{\text{HF}} - \log m_{\text{KF}}$ at $T = 400^\circ\text{C}$, $P = 1$ kbar, quartz in excess [Shapovalov, 1988].

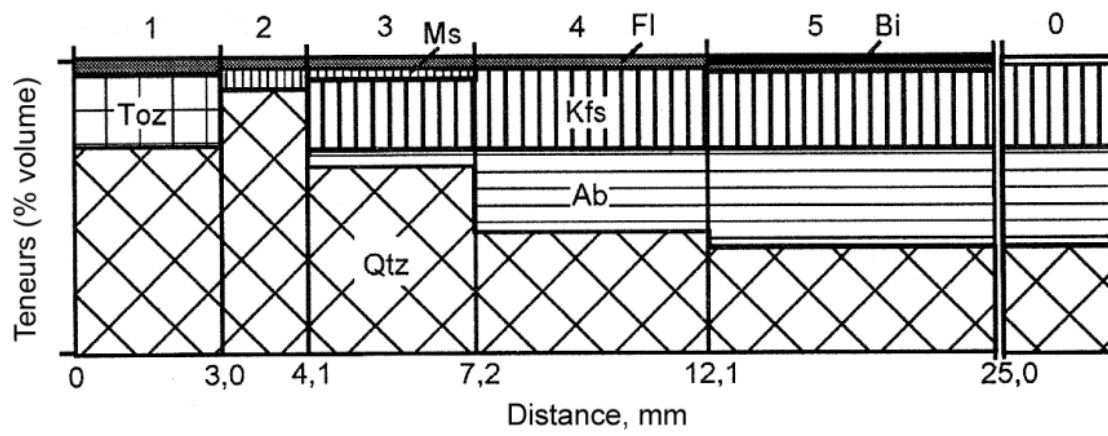


Fig. 5.7. Structure of experimental metasomatic column of greisens of quartz-topaz facies.

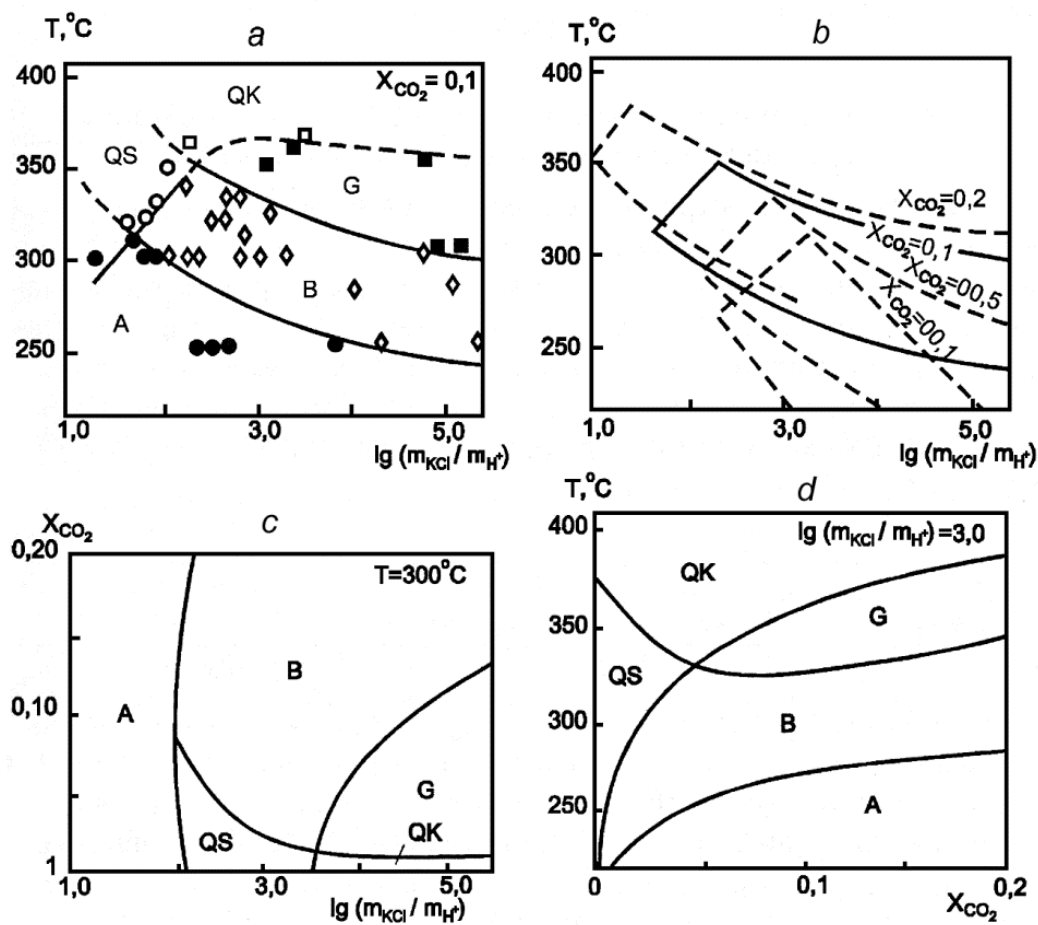


Fig. 5.8. Physico-chemical conditions of formation of beresites and other middle and low temperature acid metasomatites after data of experimental modelisation.

Fields: A of argillites, B of beresites, G of gumbeites, QS of quartz-sericite metasomatites.

Diagrams: *a*: $T - \lg(m_{\text{KCl}}/m_{\text{H}^+})$ at $X_{\text{CO}_2} = 0,1$; *b*: $T - \lg(m_{\text{KCl}}/m_{\text{H}^+})$ for fields of beresites at various values of molar fraction CO_2 in $\text{H}_2\text{O}-\text{CO}_2$ fluid ($X_{\text{CO}_2} = 0,01; 0,05; 0,1$ and $0,2$); *c*: $X_{\text{CO}_2} - \lg(m_{\text{KCl}}/m_{\text{H}^+})$ at $T = 300^\circ\text{C}$; *d*: $T - X_{\text{CO}_2}$ at $\lg(m_{\text{KCl}}/m_{\text{H}^+}) = 3,0$; $P_{\text{H}_2\text{O}+\text{CO}_2}$ everywhere equal to 1 kbar.

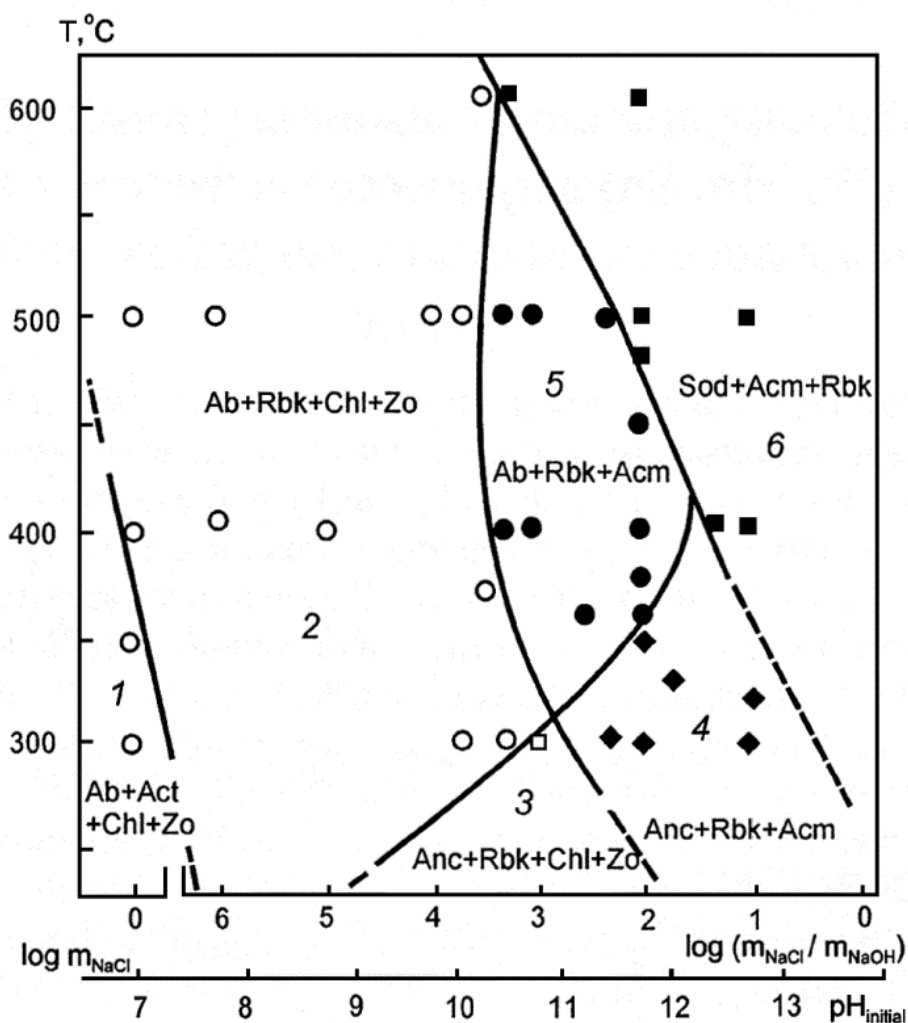


Fig. 5.9. Physico-chemical conditions of formation of alkaline sodic metasomatites after experimental data [Zaraisky et al. 1984].

$P=1\text{Kbar}$, $m_{\text{NaCl}} = 1,0m = \text{const}$, $t = 336\text{h}$; the solution quartz undersaturated, initial rock: granodiorite. Symbols indicate position of runs in coordinates $T = \log(m_{\text{NaCl}}/m_{\text{NaOH}})$. 1-6: fields of formation of various types of alkaline sodic metasomatites for which are indicated on the diagram typical parageneses of inner zones of experimental columns: 1- albite propylites; 2- albite riebeckite metasomatites; 3 analcime-riebeckite metasomatites; 4- analcime-riebeckite-aegirine metasomatites; 5- albite-riebeckite-aegirine metasomatites; 6- sodalite-aegirine-riebeckite metasomatites.

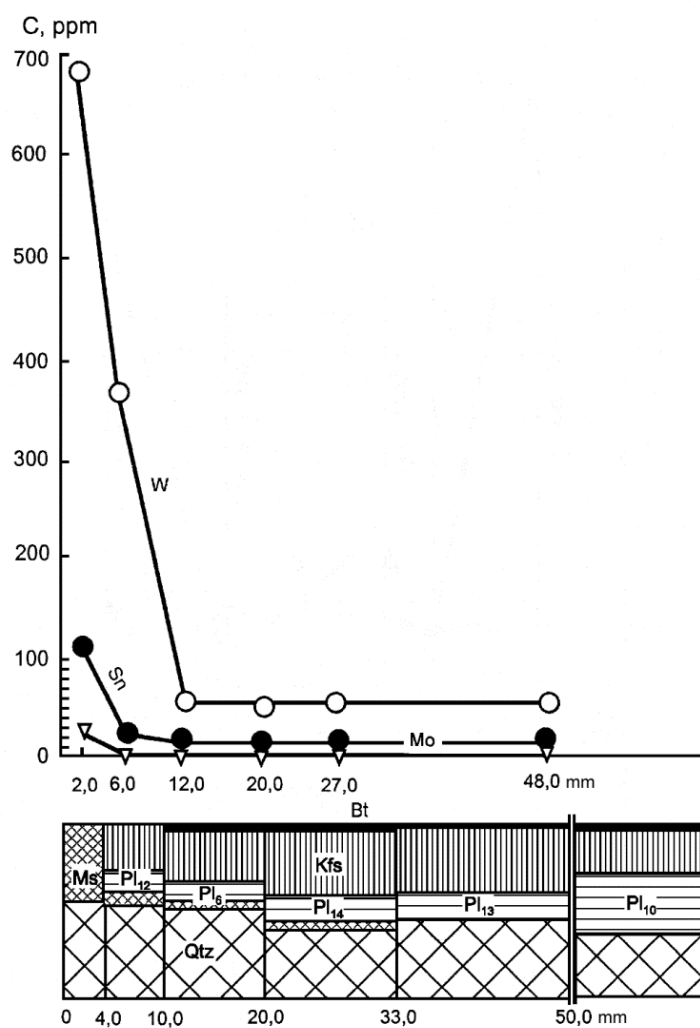


Fig. 5.10. Depositions of W, Sn and Mo synchronous with experimental greisenization of leucogranite at $T=400^{\circ}\text{C}$, $P = 1\text{Kbar}$, $t = 336\text{h.}$, solution $1\text{m}_{\text{KCl}} + 0,05 \text{ m}_{\text{HCl}} + [\text{Wlf}, \text{Cas}, \text{Mlb and Qtz}]$.

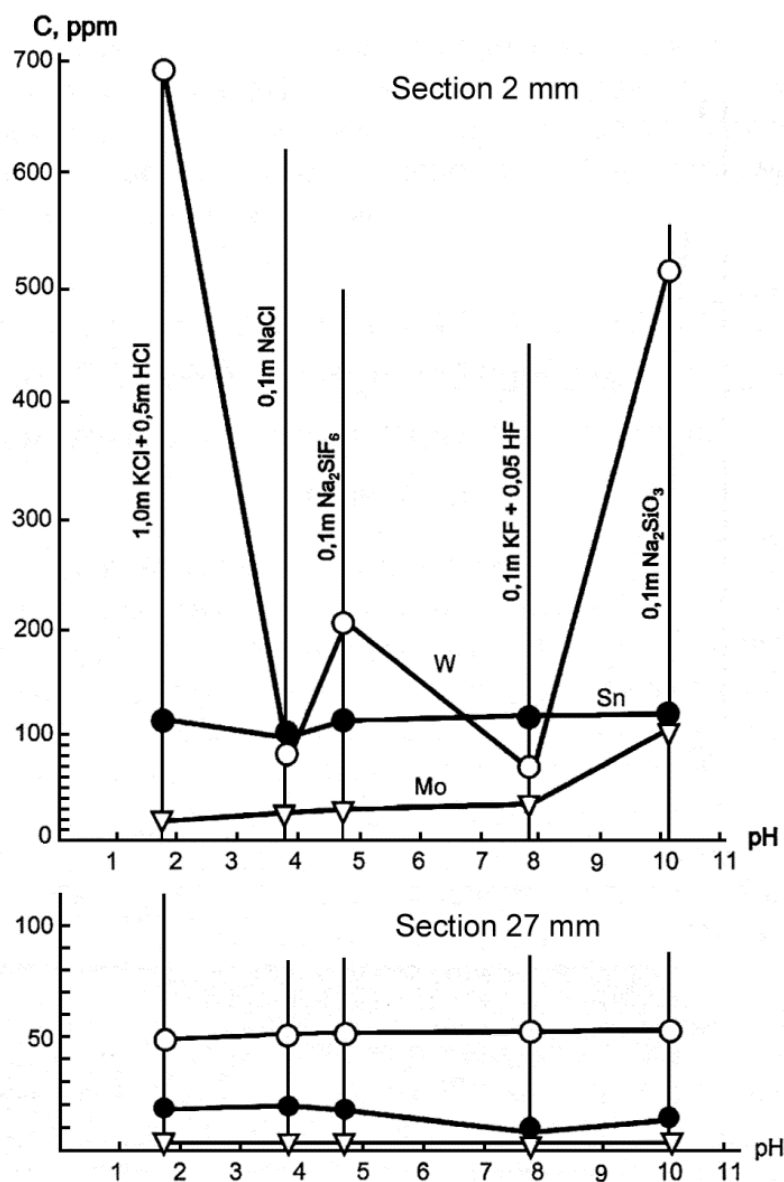


Fig. 5.11. Dependence of W, Sn and Mo content versus chemical composition and pH of solution in experimental columns of greisenization and alkaline sodic metasomatism of leugranite at $T = 400^{\circ}\text{C}$, $P = 1\text{Kbar}$, $t = 336\text{ h.}$, solution + [W, Cas, Mlb and Qtz]

Part II

Metasomatism, magmatism and mineral formation

Chapter 6

Theoretical aspects of the genetical link of metasomatism, magmatism and mineral formation

The tight spacial link between products of metasomatism, magmatism and mineralization has served as basis of the concept, now traditional, of so-called hydrothermal mineralization, tightly linked with magmatism. According to this concept, consolidation of intrusions, accompanied by concentration in residual melts of ore metals, brings about a separation of metalliferous solutions enriched with these metals, which solutions, penetrating the fissured zones of consolidated parts of the intrusions and their enclosing rocks, form in them metalliferous veins and metasomatic ore deposits surrounded by a perimetalliferous aureole of altered enclosing rocks. In support of this concept have been adduced data on general hydrothermal alteration (perimetalliferous metasomatism) of country rocks containing ore veins, and on the zonal disposition of metal ores with regard to ore-bearing intrusions, reflected in the well-known scheme of ore-zoning of Emmons.

However, there were always doubts about the effectiveness of the simple scheme proposed above. They are based on data about the low solubility of ores in hydrothermal solutions. Already in the early twentieth century V. Lindgren, notorious researcher in auriferous deposits, wrote that for the formation of the Mother Lode (in USA), a vein very rich in gold reserve, it was necessary to have a volume of solution almost equal to that of the Mediterranean sea. In order to cancel this contradiction a few hypotheses have been proposed. It was alleged that colloidal solutions may contain great concentrations of ore components and massively deposit them at crystallization. But it remained unclear from whence

and how the colloidal solutions had drawn the metals. Besides, their extent is limited, on the whole, to objects of near-superficial and subvolcanic facies of depth. Even in these conditions most ores of collomorphic texture, considering the result of crystallization of colloids, have in fact deposited from veritable solutions. Another possibility of obtaining high concentration of metals is included in the formation of organometallic complexes. Such complexes have been synthesized in laboratory and observed in natural objects. Apparently, the role of organic compounds in the extraction of metals and in their concentrated transfer is considerable in the formation of stratified lead-zinc ores from brines of the type of Cheleken (Turkmenistan) and the Mississippi valley (USA). In the typical hydrothermal ore deposits is also observed the presence of organic material filling up cavities and fissures in vein minerals and methane in fluid inclusions. However, their quantity is in most cases not sufficient for the formation of huge ore deposits.

Finally the model of recycling has recently become popular, i.e., the model of repetitive convection of the solution. According to this model hydrothermal ore deposits are formed in a zone of action of permanent circulation of subterranean waters on the type of the “Benard cell” convections. Such cells are formed on the roof of a magmatic chamber owing to a vertical gradient of temperature. The heated subterranean waters remain aggressive and dissolve the rocks’ components, including metals. Owing to difference of density with the cold water, the hot ones rise to the top and cool down, precipitating an ore load, and the cold jet settles down beneath. The repeated return of waters to the cell gradually accumulates in the zone of cooling an ore mineralization, requiring no supernatural volume of solutions. A similar model has been elaborated, for instance, for the circulation of submarine waters in zones of oceanic rift, and then extended to stratified sulfurous (pyrite) deposits and even to a few veinous ones. The weak point of the hypothesis is that in the given mechanism the origin of the metals is found exclusively in the rocks, in the immediately contiguous deposit. Such an assumption is contradicted by the presence in the ores and perimetalliferous metasomatites of elements clearly introduced from a deep magmatic source and practically absent in the enclosing rocks. For instance, some types of epithermal ore deposits of gold are characterized by tellurium, selenium, vanadium and chrome, which do not exist in enclosing acid and intermediate volcanic rocks. There is usually a high content of mercury in the sulfide pyrites and veinous sulfide deposits. Analysis of paragenesis of metasomatic minerals and of composition of fluid inclusions shows a high fugacity of carbon dioxide in the zone of ore deposit, that cannot be explained by the composition of underground waters. Finally, isotopic composition of oxygen and hydrogen of metalliferous and metasomatic fluids in epithermal deposits testifies to a significant part of magmatogene water in the fluid on deep horizons. These facts, which do not deny the participation of convective

phenomena in the general process of formation of ore deposits, testify to an addition of metals in the zone of ore deposition by a magmatic fluid. The problem therefore of explaining the conditions of separation of metals from the magma and their transfer by a magmatic fluid remains topical.

Lately, in connection with various experiments on the distribution of ore metals in systems of the type of silicate melt-hydrothermal solution, there appeared the possibility of an alternative hypothesis on the formation of an ore-concentrating fluid, canceling many contradictions. These researches have shown that in the most varied compositions of silicate melts and hydrothermal solutions, ore metals concentrate preferably in silicate melts and are practically not extracted from their aqueous solutions. Therefore separation of hydrothermal solutions from residual melts is not accompanied by an ore-concentrating effect, with which would possibly be linked the formation of huge ore deposits. In other words, we encounter the same problem of “ocean of solutions” necessary to extract from the magma a notable quantity of metals. To take such a quantity of water from magmatic chambers is impossible, due to the limited solubility of water in silicate melts, but production of water in magma from enclosing rocks is a process thermodynamically impossible. The point is that water fugacity increases with temperature. Therefore it is greater in silicate melt than in less heated enclosing rocks, and in a contact zone arises a water withdrawal in the direction of its decreasing fugacity, i.e. from magma into enclosing rock. Theoretically possible is the absorption of water from enclosing rocks of “dry” (containing no water) magma, but in nature, metalliferous granitic magmas are, as a rule, water-saturated.

Experimental data show that in order to obtain effective ore extraction from silicate melts, introduction into the system is necessary, of salt components (chloride, fluoride carbonate, etc.) in sufficient quantity to isolate them in independent fluid-melting dense phases. These dense phases also appear, in opposition to strictly hydrothermal veritable solutions, as concentrators of ore metals, effectively extracting them from silicate melts. As an example have been given on fig.6.1 and table 6.1 experimental data on the distribution of lead and zinc amid granite melts, a dense chloride salt phase and an aqueous carbon dioxide hydrothermal solution.

From the adduced data it can be seen that the dense salt phase in this system serves as unique effective concentrator of ore minerals, and that with its separation from the melt may be linked a process of formation of ore concentrations. Analogous data have been obtained on fluoride melt phases, extracting tungsten from residual granitic solutions (fig.6.2, table 6.2).

Table 6.1. Distribution of lead and zinc between granite melt, salt and hydrothermal phase of heterogeneous fluid(H₂–CO₂–NaCl) after [Chevychelov, 1992]

Composition of fluids, % mol.		Granite melt, % weight		Phase saline % weight		Hydrothermal solution % weight	
NaCl	CO ₂	Pb	Zn	Pb	Zn	Pb	Zn
53	-	0,07	0,12	1,20	1,60	-	-
0,9	-	0,09	0,08	-	-	0,23	0,18
32	-	0,03	0,03	0,42	0,25	-	-
0,6	-	0,03	0,03	-	-	0,10	0,04
52	10	0,03	0,04	1,00	0,80	-	-
1,0	20	0,23	0,08	-	-	0,35	0,10
47	18	0,02	0,06	1,20	1,35	-	-
0,8	29	0,16	0,10	-	-	0,19	0,17

Table 6.2. Initial (In) and medium composition (at % of metals) of phases I–V of fluorid granitic systems with different salt additions

Salt composition	Phase	Si	Al	Fe	Mg	Ca	Na	K	W
NaF	Initial	49.41	11.43	1.12	0.82	1.28	31.19	3.78	0.79
	I	57.89	12.28	1.14	0.21	0.44	23.16	4.40	0.18
	II	57.30	12.01	1.61	0.07	0.43	24.18	4.31	0.09
	III	2.39	9.43	0.17	10.06	23.10	43.09	5.54	6.22
	IV	3.71	9.53	0.13	7.60	15.99	54.48	5.58	2.70
	V	9.91	8.08	0.36	3.06	23.44	39.35	6.70	9.10
K ₂ SiF ₆	I	58.46	11.53	1.13	0.79	1.30	4.42	21.42	0.96
	II	64.11	11.86	1.44	0.85	0.10	3.27	17.90	0.47
	III	62.88	11.96	1.31	0.31	0.16	3.80	19.09	0.49
	IV	2.01	11.07	0.44	8.37	17.45	21.25	33.43	5.98
	V	6.18	12.56	0.38	7.51	17.33	20.4	33.05	2.59
	V	16.21	10.94	0.58	3.68	11.54	18.88	29.48	8.69
LiF+K ₂ SiF ₆ + NaAlO ₂	I	53.57	19.78	1.15	0.82	1.32	12.53	9.84	0.99
	II	63.35	17.23	1.24	0.00	0.19	7.56	10.31	0.12
	III	59.33	7.10	1.19	0.45	0.69	9.94	10.87	0.43
	IV	3.18	12.78	0.19	11.55	14.88	41.07	7.48	8.87
	V	7.35	13.67	0.15	15.13	9.47	42.82	6.66	4.75
	V	7.02	8.33	0.20	13.03	20.82	31.98	7.40	11.22

LiF+ K ₂ SiF ₆	I	62.35	13.30	1.32	0.92	1.49	5.05	14.51	1.09
	II	67.68	13.20	1.93	0.20	0.07	2.45	14.30	0.17
	III	57.77	17.65	1.79	1.65	2.88	7.66	9.94	0.66
	IV	4.51	16.75	0.47	6.39	13.90	23.04	30.01	4.93
	V	1.77	21.61	0.25	6.63	1.32	21.42	44.37	2.63
LiF	I	0.62	15.26	0.73	8.53	13.00	25.78	25.23	10.95
	II	67.50	15.65	1.58	1.09	1.75	6.01	5.14	1.28
	III	71.51	15.63	1.78	0.00	0.19	5.47	5.38	0.04
	IV	70.00	16.30	1.82	0.23	0.33	6.00	5.27	0.07
	V	5.27	4.01	0.37	10.07	39.03	11.36	0.65	29.24
	I	4.42	8.37	0.20	15.93	29.89	22.98	1.53	16.18
	II	2.12	4.14	0.00	7.37	33.88	14.62	0.69	37.18
	III								
	IV								
	V								

Those experimental data attest to the fact that fluids separate from residual melts only in case of development in them of a heterogeneity, i.e. of their dissociation in a salt phase and a hydrothermal solution, are they capable of effective ore extraction. In that case the fluid's heterogeneity determines two independent lines of evolution in the formation of ore deposits: the line of premetalliferous metasomatism and the line of formation of proper ore bodies, superimposing themselves on the metasomatically altered rocks. The usual delay between ore emplacement and metasomatism is explained by a higher mobility of hydrothermal solutions compared to more viscous dense phases rich in metals and forming in the end a great variety of ore bodies. Melts departing from them are formed in processes of development of liquid immiscibility in the residual magmas. In determined conditions their metalliferous specialization may form later on as a result of superimposition of metamagmatism on a liquefying melt, i.e. change of composition of magma owing to filtration through them of flows of transmagmatic fluids. This effect is most brilliantly manifested in sulfurization of basic magmas and formation of copper-zinc and copper-nickel magmatic deposits. An application of the hypothesis to ore deposits is examined below on examples of deposits of pyrites, rare metals and veinous gold.

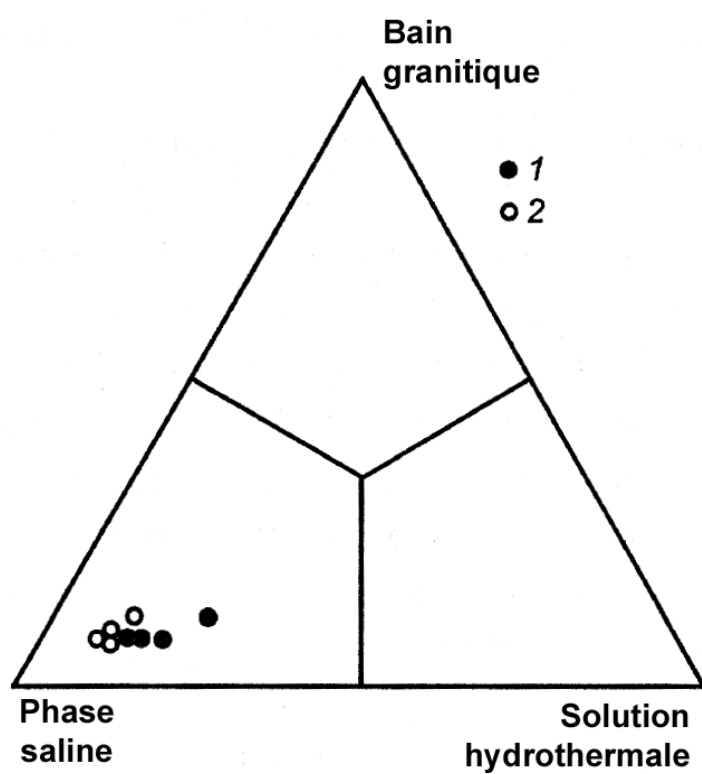


Figure 6.1. Distribution of lead (1) and zinc (2) between granite melts, salt phase and aqueous and CO₂ hydrothermal solution, after data of table 1 [Chevichelov, 1992]

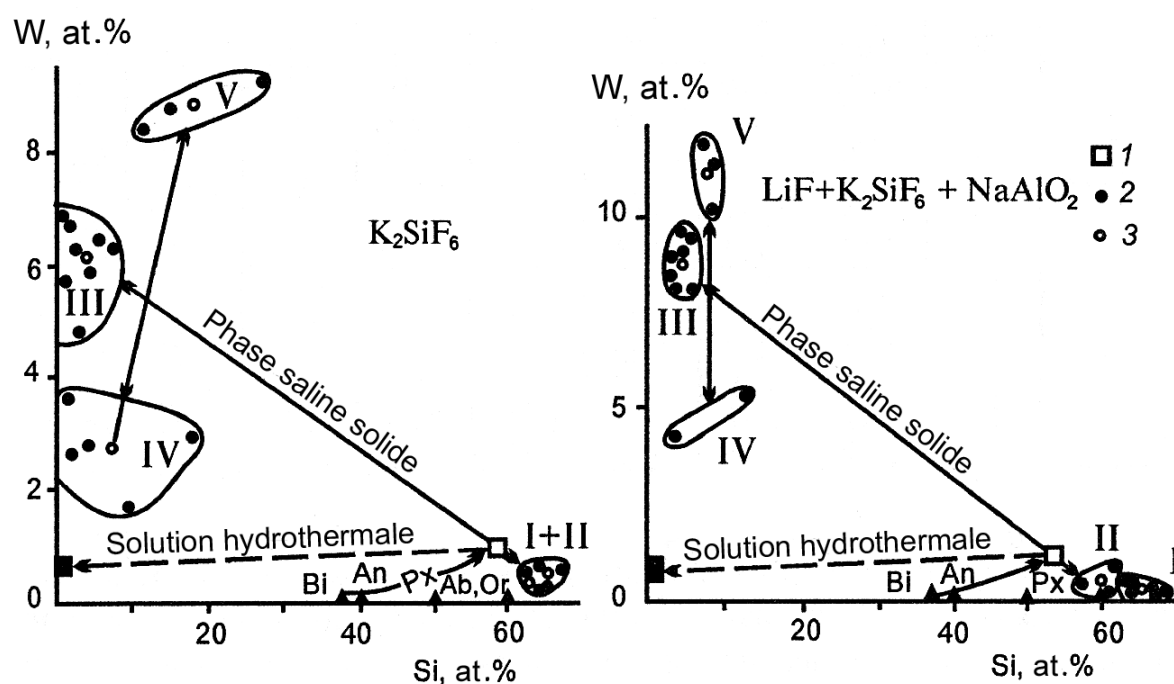


Fig. 6.2. Diagram of atomic percentage of metals, illustrating effectiveness of salt extraction of tungsten relatively to hydrothermal solution.

Lower arrow illustrates crystallization accumulation in residual melt of silica and tungsten at separation of minerals: biotite (Bi), anorthite (An), pyroxene (Px), albite (Ab) and orthoclase (Or). 1, residual granite melt; 2-3, composition of melt phases, formed at its separation (2 isolated analysis, 3 average analyses); I-II silicated phases, III-V salt melt phases (tungsten concentrations).

Chapter 7

Spatial and temporal correlations of metasomatites, ores and magmatic formations.

Metasomatism, magmatism and ore deposits usually are phenomena tightly linked in space. In relation to magmatism one distinguishes between metasomatism at magmatic (progressive) stage, accompanying magmatic replacement of enclosing rocks; metasomatism at postmagmatic stage; metasomatism the link of which with magmatism is non-evident or non-existent. Of the greatest interest from the point of view of ore detection are the products of postmagmatic metasomatism, and metasomatites at the magmatic stage are not themselves metalliferous. A particular group of metasomatites, revealing no clear links with magmatism, is represented by low temperature argillitized rocks, for examples bentonites. Usually they contain no mineralization of metals, but themselves serve as mineral resources. However, examples are described, in the literature, of copper (chalcopyrite) mineralization included in bentonites and having presumably a hydrothermal origin.

Research on the correlation of metasomatism and ore deposits is one of the main directions in the theory of metasomatic processes, owing to the general interest for metasomatic rocks, thanks to the presence in them of ores of non-ferrous and precious metals. This gives the problem an economic aspect and some genetic uncertainty, because criteria of definition of an ore include industrial conditions and technological possibilities, which vary in time. There exist types of metasomatically altered rocks containing no mineralization, known as “barren rocks”. They are products of subvolcanic argillization in the solfatara fields on volcanoes and areas of unloading of thermal volcanic waters resulting from halmyrolysis of basalts on the oceanic bottom, metasomatites at magmatic stage, forming ahead the front of magmatic replacement of rocks (except magnesian skarns, on which are superimposed postmagmatic hydrothermal processes). Barren also are metasomatites formed in local matter

transfer in a process of regional metamorphism. In this case can only occur either a dispersion or a redistribution of previous metal deposits.

A particular group of metasomatic rocks are those which present themselves as mineral resources, such as for example some facies (zones) in columns of metasomatic zoning. To them are related in argillized rocks and secondary quartzites, agalmatolites (kaolinites), extracted as building stones; alunites as raw materials for production of alums; corundum and alunite, for the production of aluminum; bauxite in crusts of weathering; talc in contacts of serpentinite massifs; apatite in massive alkaline and alkalino-ultrabasic rocks.

Metasomatic rocks presenting a potential ore aspect are subdivided, concerning ore, into voluminous preore metasomatites, local protoore metasomatites and periveinous synore metasomatites. Postore metasomatites are uniform, usually presenting veinlets of calcite, quartz or zeolite, and yield little information about ore-metasomatic processes. A detailed characterization of metasomatites and the mineralization they contain is adduced in description of the corresponding families, but in the present section are given the general regular correlations between metasomatites and ore.

To preore metasomatites correspond products of hydrothermal transformation of relatively great volumes of rocks (pervasive metasomatism) without immediate link with ore deposits. Preore metasomatites, not being themselves ore carrying, embody much later, generally acid metasomatites, containing ore mineralization.

The most typical example of preore metasomatites is the *family of propyllites*. The peculiarity of propylitization consists in the fact that it begins on the stage of introduction of magma and its replacement of enclosing rocks, but it continues to a stage of cooling down of intrusion and separation from it of postmagmatic hydrothermal solutions. Propylitization occupies a volume of rocks equal to the dimensions of the ore field. Mineralization, surrounded by perimineralisation of altered rocks, is localized in propylitized rocks in the form of veins or of linear zones of veinous-disseminated mineralization, as, for instance, in the gold-quartz deposit of Mnogovershinnoe in Low Priamour (fig.7.1).

The most ancient potassium-argon age of biotite from the lower zone of propyllites in this deposit is between 10 and 8 million years, but the age of sericite, accompanying veins of ore-quartz, is between 72 and 75 million. Examples of less wide-spread mineralization are dispersed in the volume of propylitized rocks. In those examples the age relations of propyllite and ore are indistinct, but usually, one can observe replacement of chlorite and albite of propyllites by sericite and signs of quartzification, i.e. signs of perimetalliferous acid metasomatism superimposed on propylites.

Skarns are another example of pre-ore metasomatites. Their formation is much less voluminous, their thickness does not exceed a few decameters, but

their extent, as a rule, is of several hectometers. Mineralization is usually separated in time from skarnification processes by those of amphibolization (in magnetite deposits) or more distinctly by the appearance of acid metasomatism of beretization type (in polymetallic and gold deposits) and greisenization (in tungsten deposits). Exceptional are magnetic ores in magnesium skarns at the magmatic stage, synchronous with skarn formation. Some researchers [Ezhov, 1994] consider sulfide mineralization interspersed in skarns, to be synchronous with skarn formation, for the reason that in some cases no signs are observed of replacement by sulfides of the skarns' pyroxenes and garnets. S.V.Ezhov corroborates that assumption by his own experiments [Ezhov & Zarausky, 1995], in which sulfides were deposited in a determined zone of the skarn column at the time of the latter's formation. These experiments show the possibility, in principle, of sulfide deposits together with skarn minerals, if the skarnifying solution contained a sufficient metal concentration and possessed a high enough activity of sulfidic sulphur. In natural conditions, however, skarnifying solutions have a clearly expressed chloridic character and a low concentration of sulphur anions. Sulfur activity increases in a postskarn process at lower temperature, when a great mass of sulfides precipitates. There is besides no sufficient reason to isolate a disseminated mineralization from a distinctly postskarn vein mineralization.

The protracted live of a hydrothermal system that is reflected in the presence, besides directly perimetalliferous metasomatites, of preore ones, including at magmatic stage, proves to be a compulsory feature of big deposits. It is linked with the fact that in the long evolution process there occurs "maturation" of the magmatic-hydrothermal system, which in the last stages of evolution acquires the capacity concentratingly to deposit a great mass of ore matter. "Maturation" includes a huge differentiation, in the magmatic chamber, of a complete transformation of the system in its transfer from tendency to eutectic to liquation with formation of ore-concentrated salt melts and metasomatizing fluids of low density. Therefore, in particular, propylites, although barren in themselves in most cases, are signs (together with the presence of other metasomatites) pointing to ores of non-ferrous and precious metals.

Protoore metasomatites are more varied than the preore ones. To them are related periveinous beresites, listvenites, rocks with quartz-sericite and quartz-chlorite sericite, argillised rocks, gumbesites, acites, greisens. Under the action of acid solutions on silicic rocks (rhyolites, granites) arise secondary quartzites containing scattered mineralization of molybdene (deposits of molybdene-porphyry type). In the enumerated types of metasomatic rocks may appear moreover products of specific processes, linked with an addition of hydrothermal boron (tourmalinization), fluor (replacement of calcic plagioclase

by fluorite), vanadium and chrome (formation of roscoelite and fuchsite), sodium (albitization), potassium (adularization).

Beresites border mineralized bodies of uranium, gold and polymetallic deposits. Their potassium-argon age, as a rule, coincides, reserving errors of method, with the age of ore, determined by inclusion of sericite in the sulfides or segregation of adular in the ore vein. In the geological context, however, it is established that perimetalliferous metasomatism occurred earlier than the ore deposition. Beresitized rocks are cutted by a net net of quartz veinlets with ore minerals, the last replacing carbonates and early pyrite of the beresites. Moreover, ore minerals often appear together with berthierite (or ferriferous chlorite), ferriferous magnesian carbonate or quartz, with which also are replaced sericite and carbonates of beresites. Thus are formed protoore metasomatites, although not much on the geological scale, but earlier than ore.

Quartz-sericite and quartz-sericite-chlorite perimetalliferous rocks in pyrite deposits form under-ore metasomatic aureoles, nearly at the same time with the deposition of massive sulfides. This is established by geological correlations on recent deposits of Kuroko type and on example of contemporaneous sulfide formation in the “black smokers” on oceanic bottom (fig.7.2). In ancient pyrite deposits it is possible to distinguish the spatial distribution of quartz-sericite metasomatites with regard to ore from their reorientation in the process of metamorphism and folding. In the pyritaceous polymetallic deposits of Metalliferous Altai, forming in the regional shear zones, V.B.Chekvalidze [1981], together with sub-ore metasomatic zones of acid metasomatites, distinguishes over-ore zones of re-deposition taken out of sub-ore zones of foundation (zones of chloritization, carbonatization, albitization). In that case, mineralization constitute one of the zones of the metasomatic column.

In the molybdenum –bearing porphyric deposits protoore acid metasomatism occupies a greater volume of rock in the endocontacts of granitic porphyric intrusions. Volume variation is characteristic of preore metasomatism, but in the given case the mineralization deposit is nearly contemporaneous with silicification. As a result of metasomatism, essentially quartzitic rocks are formed with dissemination of minerals rich in aluminium (corundum, andalusite, diaspore, pyrophyllite). Above these rocks, in the fracturation zones, is superimposed a streaky disseminated molybdenite mineralization accompanied at places by sericite. In the deep parts of metasomatically transformed granites extends a zone of quartz-orthoclase metasomatites, containing quartz-orthoclase veinlets with molybdenite. Detection of high-aluminous secondary quartzites is not in itself a sufficient sign to confirm the presence of molybdene mineralization. There exists a group of secondary quartzites that do not contain ore mineralization. They differ by the presence in them of huge isolated high-aluminous minerals (corundum, diaspore) that are on industrial scale and are extracted as useful minerals. Furthermore, another difference consists in the fact

that secondary quartzites of porphyric deposits are formed under the action of solutions with a much higher fluorine activity contributing to composition of mica and fluorite, than high-aluminous “oreless” quartzites forming under the influence of substantially chlorinated solutions.

In relation with more fundamental porphyric intrusions of alkali-granodiorites or syeno-diorites are formed ores of the *copper-porphyric type*. Protoore metasomatism in such deposits differ of the above characterized by a much weaker degree of silicification. An important type of change is sericitization up to formation of quartz-sericite rocks (“phyllites”). The morphology of ore mineralization in them is analogous to that of molybdenum-porphyric ores, but the time of ore deposition approaches that of sericitization. Not only does sericite replace magmatic minerals in great volumes of rocks (pervasive sericitization) but it directly accompanies segregation of copper sulphides appearing as protoore as well as synore mineral.

Greisenisation of rocks occur either as periveinous alteration along veins of quartz and greisens, or as volume alteration in cupolas of hypabyssal and subvolcanic granitoids. Periveinuous greisenisation is protoore relatively to inclusion in veins of mineralization of tin and tungsten, but it is almost simultaneous with deposition of topaz and beryl in the veins. Volume greisenisation (fig.7.3) in granite cupolas presents itself as preore alteration of rocks.

Synore (ore-accompanying) metasomatism, differing from all types described above, are mostly monomineral and consequently have no zonal structure. They represent the result of reciprocal direct reactions of ore-fluids with a varying surrounding, but their expansion is strictly limited by contacts of grains or grain aggregates of ore minerals, contacts of ore veinlets and their lode wall. As examples may serve ore breccias in the gold-telluride deposits of Kochbulak (Uzbekistan), in which fragments of surrounding rocks, cemented by sulfide, cements are completely replaced by sericite or fringes of ferri-ferous chlorite around thin veins of carbonate with native silver and silver arsenides in the silver-arsenidic deposit of Aktepe (Uzbekistan) (fig.7.4). The strongly limited extent of synore metasomatites within the boundaries of ore mineralization and the absence, in most cases, of metasomatic zoning attests to the specific properties of ore-carrying fluids, to their limited capacity, in particular, to percolate through rocks. It may finally be linked to their great viscosity compared to protoore solutions.

Synore metasomatites formed at high temperature may coincide in composition with protoore metasomatites. For instance, in endocontacts of a quartz-feldspar zone of contact metasomatism in molybdenum-porphyric deposits molybdenite forms metasomatic veinlets together with feldspar and quartz. More varied are synore metasomatites at middle or low temperature, amongst which the most widely spread are those of amphibole, chlorite,

carbonate, potassic feldspar, albite, sericite and quartz. Feldspar metasomatites are particularly interesting as they are accompanied by the most varied mineralization and are formed in a wide range of temperature. In pegmatites, albitization is accompanied by mineralization of rare metals (Ta, Nb, Be). The process occurs in strict conditions of high alkalinity, in which even quartz is replaced by albite. Quartz-feldspar metasomatites of molybdenum ores are formed in a less alkaline surrounding and are accompanied by granite bleaching. In mediothermal gold deposits veinlet metasomatic albitization is masked in places by an increased concentration of metal, but in epithermal deposits potassic feldspar is more significant: places of rock adularization and development of adular in a quartz-ore vein usually coincide with ore pillars and nests of rich ores of gold and silver.

Carbonates and chlorites of synore metasomatites are distinguished by high (sometimes very high) ferruginous character and increased manganese content. Greater manganese content of these minerals is particularly characteristic of ores of galenite-sphalerite, silver-polymetal and gold-silver. Apart from the composition, the distinctive peculiarity of minerals of synore metasomatites is their metastable structural state. So, along with chlorite and sometimes instead of it, there occurs berthierite in the metasomatites. This mineral is, as to composition, identical with chlorite, but at the basis of its structure lies a single-layer packet with interjointal distance of 7Å, whereas chlorite is made up of double-layer packets with interjointal distance of 14Å. Geological observations and experiments have shown that the structure of berthierite is metastable and that under thermal influence or simply in course of time it passes to the stable 14Å structure of chlorite. Sericite presents the structural polytype 1M or 1M+2M mixture. The polytype 1M, as experimentally established, is metastable and under thermal influence passes to a stable modification. The development of metastable minerals in ore associations and ore-accompanied associations expresses the strongly unbalanced character of the process of ore deposition from oversaturated fluids. This also appears in the appearance of autoorganization of a hydrothermal-ore system, bringing about formation of rhythmic-banded ores and synore metasomatites.

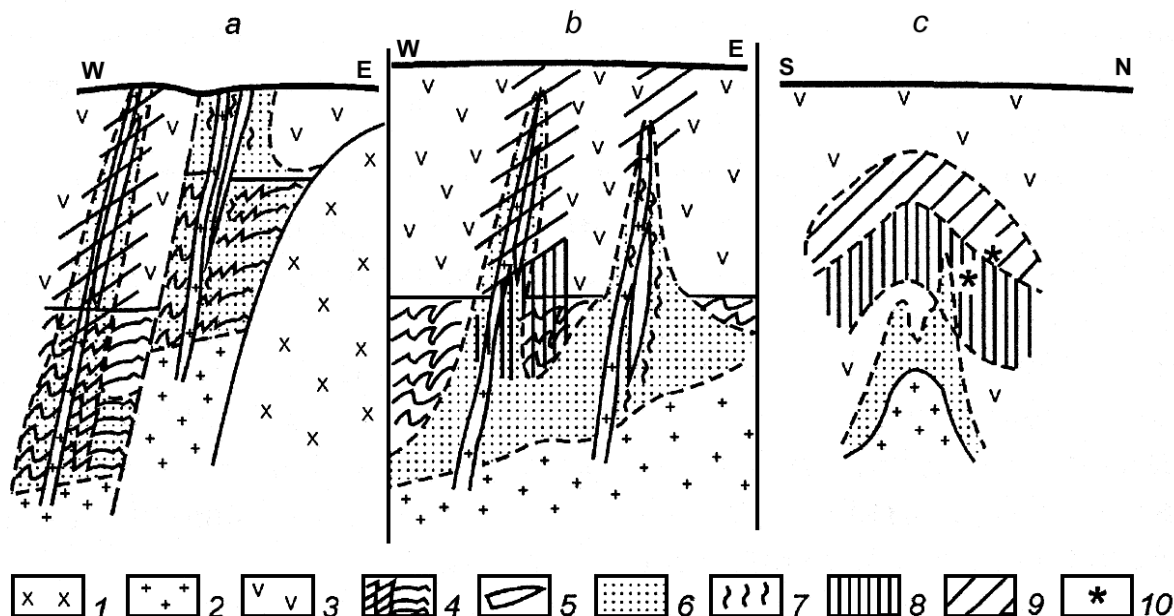


Fig. 7.1. Distribution of beresite facies on schematic geological sections across manifestations of gold mineralization.

a, b – deposit of Mnogovershinnoe (Low Priamur) (*a*, contemporary situation of ore veins, *b*, reconstruction at moment of ore formation; *b*, Angrensky gold ore region, Kochbulak and Kairagach deposits in Central Asia. 1- post mineralization of granodiorite porphyry; 2- protoore granodiorites, syenite-diorite porphyrite; 3- andesite-dacite volcanic thickness; 4 terrigene rocks of basement; 5- quartz-ore veins. 6- biotite facies of propylites; 7 – 9 facies of beresites (7- quartz-sericite, 8 quartz-calcite-sericite, 9 quartz-ankerite-sericite, 10- ore occurrences and ores).

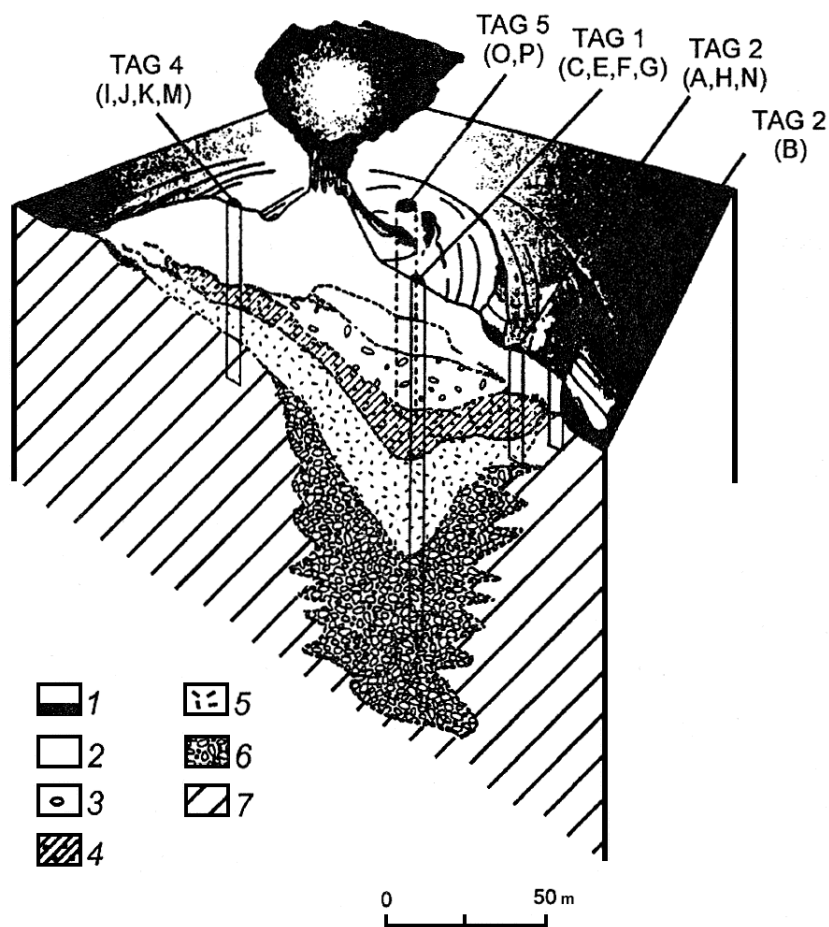


Fig. 7.2. Block-diagram and internal structure of hydrothermal spring depositing sulfides on sea bottom after data of deep water drilling [Humphris et al., 1995]

Displays of distribution and numbers of bore holes. 1 - massive pyritic breccia; 2 - pyrite-anhydrite breccia; 3 - pyrite-chert-anhydrite breccia; 4 - pyrite-chert breccia; 5 - silicification of crushed enclosing rocks; 6 - chloritized brecciated basalts; 7 - basalts

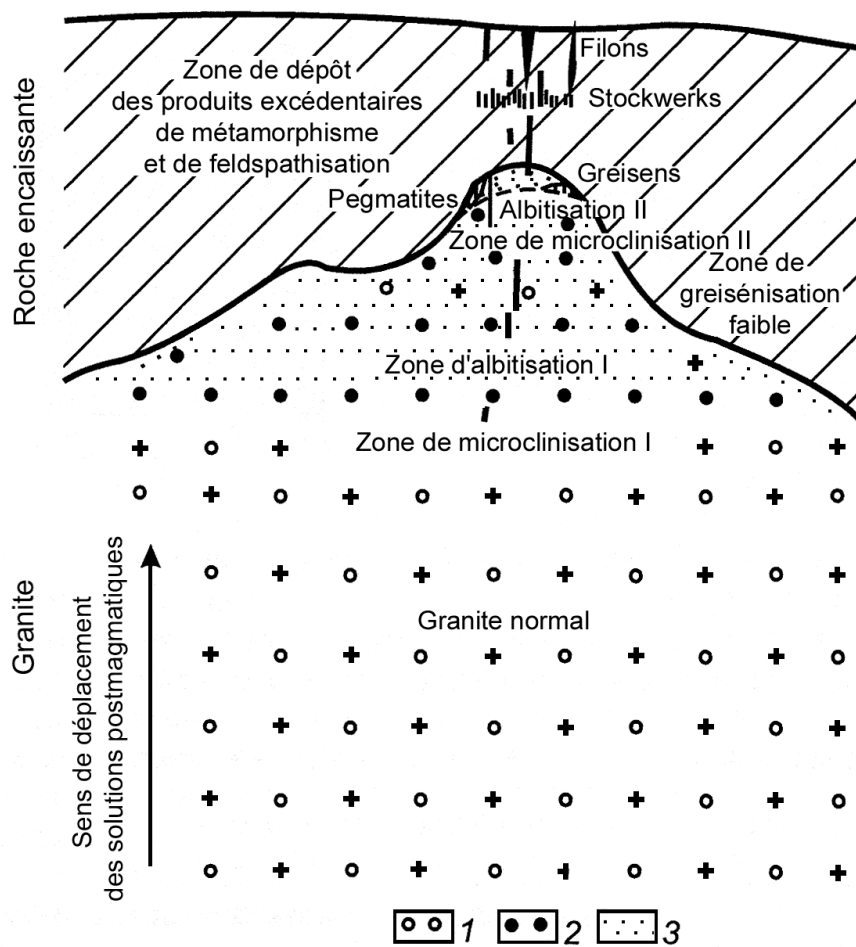


Fig. 7.3. Generalizing scheme of vertical zonation in massive greisenization of granites after [Shcherba et al. 1964].

1-3 altered granites; 1- microclinized, 2 - albitized, 3 - greisenized.

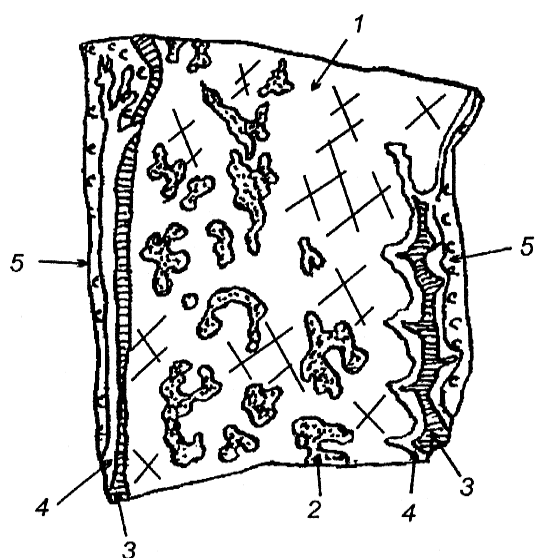


Fig. 7.4. Sketch model of ore vein with fringe of synore metasomatites from silver-arsenide ores of Aktep (Kuraminskie mountains, Central Asia).

1 - carbonate vein; 2 - arsenides and native silver; 3 - chlorite; 4 - adular; 5 - sericitized enclosing gabbro.

CHAPTER 8

Metasomatic zoning and ore zoning

Ore mineralization, as a rule, is disposed in the central part of metasomatic altered rocks, in the zone of their greatest transformation and of a most intense hydrothermal process. In some types of metasomatites ores are confined to definite mineral associations. For instance, in skarns, polymetallic mineralizations selectively replaces various pyroxenes, which is linked with greater solubility of hedenbergite in acid sulfide solutions, compared with garnet and other skarn minerals.

It is quite complicated, although not less important, to explain the correlation between vertical zoning of periorite metasomatites and ores. Important factors in the formation of vertical metasomatic zoning are temperature and fugacity of oxygen [Rusinov, 1989]. At a different depth the relative influence of these factors on mineralization is different. The role of oxygen rapidly increases in the least deep formations, where intense aeration of subterranean waters is possible. Here a change of zones (facies) is observed in the vertical direction on small distance, reflecting not only temperature zoning, but also sudden increase of oxidation degree of the forms of sulphur and iron in the solution as the surface is approached. For instance, in the epithermal gold-silver deposits may be observed upwards change of the zones: propylite with pyrite, quartz-hydromica rocks with pyrite, quartz-kaolinite-alunite rocks with hematite, monoquartzites in a vertical interval of 200 – 400 m.

More deeply, in subvolcanic and hypabyssal depth facies an important role is played by the temperature gradient. It is reflected, for instance, in shift to the surface of an epidote-chlorite facies of propylites by an albite-calcite or in shift of calcite-sericite facies of beresites by ankerite-sericite facies (cf.fig.7.4). In this figure is indicated the position of gold ore and silver-polymetallic

mineralization in aureole of metasomatic rocks in the ore region of Kochbulak-Lashkerek. The deposits are distributed in the area of development of beresitization of enclosing volcanic rocks, basically in the zone of ankerite-sericite facies (Lashkerek, Kayragach) and a calcite-sericite facies on its limit with the ankerite-sericitic one (Kochbulak). Further below, volcanic rocks underwent metasomatism of the magmatic stage and keratisation, and in this zone ore mineralization tapers out.

Other correlations of vertical metasomatic zoning and mineralization are observed on the gold-quartz deposit at Mnogovershinnoe in low Amur (see fig.7.1). Preore metasomatites are represented by propylites, in which zoning is clearly manifested: the upper zone is composed of an epidote-chlorite facies with parts of epidote-actinolite, and the lower one of a biotite facies. Abruptly declining quartz-ore veins, surrounded by protoore berezitized rocks, cut through propylites of an epidote-chlorite facies, and are deeply rooted in a biotite facies. Gold mineralization is concentrated in the veins' upper part, dispersed among epidote-chlorite propylites, and rapidly tapers out in depth in the biotite facies. Tin mineralization of quartz-cassiterite formation, coinciding with the roof of subvolcanic granitoids, on the contrary, concentrate in a biotite facies of propylites, in close contact with an intrusion. Ore bodies taper out in contact-hornfels.

These examples show that mineralization tends to localise in a determined facies of metasomatites and tapers out in a region of facial limits. As lower limit of extension in depth of gold and silver mineralization serves the biotite facies, and for tin mineralization, contact hornfels at higher temperature. In copper porphyric deposits the lower limit of chalcopyrite mineralization coincides approximately with the limit between sericite and a more deeply lying quartz-feldspar facies, and in the molybdeno-porphyric the lower limit of extension of industrial molybdenite lies in the zone of passage of quartz-feldspar metasomatites with low altered granites.

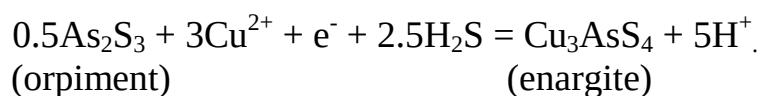
While studying ore deposits it becomes necessary to distinguish deep formation and degree of erosion of neighbouring deposits or even of ore bodies. Such distinctions are sometimes too small and do not function according to parageneses of non-metallic minerals, but are noticeable in associations of ore minerals (mainly sulfides) more sensitive to variations of physico-chemical parameters. D.S.Korzhinsky [1940] drew attention to the fact that in conditions of small depth the oxygen's fugacity is a factor of equilibrium, which is reflected in replacement of pyrothite by pyrite and of magnetite by hematite. Later research has shown coincidence at small depths of sulfides containing metals (arsenic, antimony, tellurium) in the highest positive valences. In these conditions, oxidation conditions of mineral formations are determined by oxygen fugacity, which in turn depends upon depth and degree of aeration of the subterranean waters.

The variations of oxygen fugacity, finally, are more strongly reflected in the equilibrium of sulfides and metalloxides than in the stability of rock-forming silicates and carbonates. Nonetheless, since this parameter clearly depends upon the depth of the hydrothermal process, and upon temperature, we observe some correlation between the vertical zoning of ore mineralization and metasomatic ore deposition. It is clearly possible to see this correlation on the example of correlation of extension of arsenic minerals and the acid metasomatites that enclose them in depth (table 8.1). At the basis of this table is placed comparison of two types of vertical zoning: zoning of acid perire metasomatites, determined either by temperature, or by oxygen fugacity (and, consequently, depth) of the process; and zoning of ore minerals, conserving arsenic in various valences, depending on

Table 8.1. Comparison of facies of depths of metasomatites and ores

Depth, km ($\lg f_{\text{CO}_2}$)	Facies of depth after D.S. Korzhinsky	Facies of acid metasomatites	Types of mineralisation [Shikazono, 1985] ($\lg f_{\text{CO}_2}$)	Facies of ore on degrees of oxidation
1 (-2 ÷ 0)	Superficial (without epidotes)	Kaolinite- alunitic	Au –Ag (-2 ÷ 0)	Auripigment
	Subvolcanic (without clinozoisites)	Hydro- micaceous		Enargitic ($\lg f_{\text{O}_2}$)=-35÷-42
		Ankerite- sericitic		Faded ore without enargite
2 (0 ÷ +4)	Hypabyssal	Calcite-sericitic	Pb –Zn –Mn (-1 ÷ +1)	Arsenopyritic
(+2 ÷ +8)			Cu –Pb –Zn (-0.5 ÷ +2)	

oxygen fugacity. A geological factor, uniting these two types of zoning, is depth; with the latter's increase temperature augments and so does carbon dioxide fugacity, and diminishes oxygen fugacity. The most oxidized forms of arsenic are found in mineral superficial formations in contemporary volcanoes and in zones of hypogene oxidation of ore accumulation (scorodite, orpiment) and also in upper horizons of some ore deposits of epithermal and porphyric type arising in subareal, well aerated stratas (enargite, luzonite). Passing to deeper horizons, these phases are replaced by others, realgar and faded ores, with less oxidized forms of arsenic. Enargite contains arsenic in highest valence (+5), but are not characteristic of superficial formations, where in the presence of sulphur the main form of arsenic manifestation is orpiment with a lower valence of arsenic (+3). Enargite detections in solfatare fields of volcanoes are isolated. This is explained by reciprocal electronic action of arsenic and copper: in enargite, copper is found in valence (+1) since it takes part with sulphur to oxidation of arsenic, having less affinity than arsenic with sulphur. As a result, the high valence of arsenic in enargite is determined by external oxidizing conditions and intramolecular electronic transfers. That is why enargite is formed in less oxidizing conditions than orpiment, as obvious in the reaction equation:



With increase of depth and decrease of oxygen fugacity is obtained instead of orpiment a spreading of realgar (AsS with arsenic valence +2), and in environments with copper saturated solutions, enargite is replaced by tennantite (with As⁺³). In an even more reducing milieu and at greater depth appear as main phases of arsenic, arsenides, arsenopyrites, löllingite, arsenious pyrite, i.e. minerals in which arsenic plays the role of anion with negative valence. Native arsenic is relatively rare in nature owing to its high affinity with sulphur. Its deposition from volcanic gases is due to the reducing action of arsenic at the expense of the sulphur oxidation.

Practically there exists a main vertical zoning of metasomatic rocks in the scale of ore fields and even regions. For instance, the basic classical schema of porphyric fluido-magmatic system of R. Sillitoy (fig.8.1), which develops from the metallogenetic zoning of Emmons, in conformity to a given type of fluido-magmatic systems, may serve as reliable guide in the searches of ore deposits in regions of porphyric intrusions.

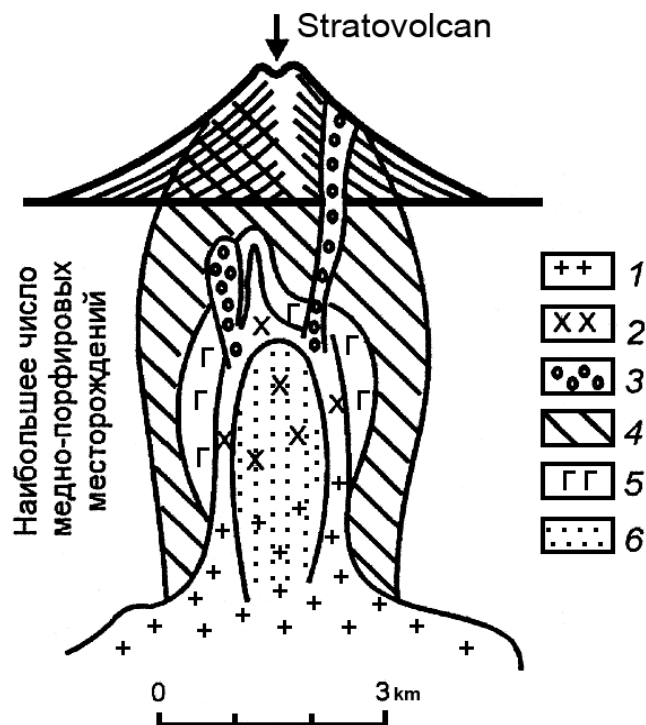


Fig. 8.1 Scheme of structure of hydrothermal magmatic systems producing Cu-Mo porphyritic deposits [after R. Sillitoe, adduced by Smirnov, 1965].

1 - granodiorites; 2 - stock of granite porphyries; 3 - hydrothermal breccia pipes; 4 - propylitized rocks; 5 - sericitized rocks; 6 - orthoclase metasomatites.

Caption in Russian (vertical axis): maximum number of porphyry copper deposits

CHAPTER 9

Magmatism, metasomatism and massive sulfide mineralization

The genetic link of pyrite ore-formation with volcanism, established through examining recent Japanese deposits (such as the so-called Kuroko ore) in comparison with ancient Ural deposits, has been traced by A.N. Zavaritsky. V.I.Smirnov especially underscored the role of submarine volcanism, accompanied with accumulation of volcanic sedimentary deposits, to which are subordinate stratiform massive sulfide deposits. Given the links with exhalation-sedimentary processes, these deposits are usually characterized by a great range of mineralization and a variety of metallic composition.

Copper-zinc sulfides occurrences on oceanic bottom are closely linked with magmatic chambers, which are situated according to geophysical data at small depths under mid-oceanic ridges. These chambers are divided into lower, ultrabasic, and upper basic parts. The basic one directly feeds the basaltic eruptions of the mid-oceanic ridges. Basalts of this type are characterized by high variation of the magnesium content (in inverse relation with content of iron, titanium and vanadium) from 16% MgO in magnesian basalts to 3-4% MgO in titanitic ferrobasalts. Magmatism is characterized by a reducing regime and relatively low fluid pressure. Crystallization temperature of the magma in these conditions is relatively high, and crystallization occurs in the zone of stability of pigeonite, which enters the composition of phenocrysts and of the matrix (type of pigeonite basalt of K. Kuno). The diagram of differentiation of magma (fig.9.1) includes fractional crystallization with formation of ferrobaltic melts, which then liquefy with separation of icelandites, ferrodacites, alkaline liparites, pantellerites and comendites. A similar separation of acid melts reflects immiscibility of pyroxene-quartz melt, characteristic only of residual magmas, rich in iron and titanium. Roman digit I on fig.9.1 indicates ferrobaltic trends of crystallization differentiation, typical of rift magmatism and conditioned by fractioning of pyroxene jointly with plagioclase. Evolution culminates in separation of ferriferous melts with formation of small volumes of rocks of average and acid composition. Exactly with this stage of evolution of

volcanic complexes, there arise, together with acid, extremely iron enriched magmas, linked with pyritic mineralization. Ferriferous magmas under the action of fluxes of transmagmatic fluids are slightly subjected to sulfurization with enrichment of copper and chalcophile metals. Amongst rock-forming minerals the plagioclase structure is the most favourable for receiving lead replacing calcium, which also determines accumulation of lead in the residual melt and its absence in pyrite ores, linked with rift magmatism. On the contrary, copper and zinc enrich residual melt. This sketch is confirmed by geochemical data on the composition of porphyrites of the Sinantchin suite in southern Sikhote-Alin [Filimonova, 1988]. Content of metals in these porphyrites and their plagioclase phenocrysts (digits in parentheses) consist in g/t: Cu = 40 (20), Zn = 100 (10), Pb = 15 (30). Consequently, lead was chiefly captured by phenocrysts of plagioclase, whereas copper and zinc accumulated in the residual melt.

On fig.9.1 is distinguished, on principle, the differentiation trend II, linked to crystallization and fractionation of olivine. This trend assists increase of water pressure in the magmatic chamber, reducing, according to experimental data, crystallization of plagioclase and broadening the crystallization field of coloured minerals, specially olivine. This trend may be called andesitic since olivine fractioning brings about a rapid accumulation of silica in the residual melt and replacement of basic by intermediate magmatism. It is characterized by transition from a regime of extension to one of compression and magmatism of orogenic type. Despite the difference, this trend is completed, like the ferrobasic one, in the splitting of melts, but with formation of a great volume of acid magma and of a relatively small one of iron rich melts, submitted to sulfurization, which serves as basis of sulfides formation in the basalt-andesite trend of evolution. In this trend, plagioclase fractioning was limited; therefore, lead with zinc accumulated in the residual melts, determining a specific character of pyritic ores, linked with that magmatism. An example of development of the andesitic trend is the volcanic complex of Mutodjar (South Ural) [Marakushev et al., 1993], but an example of more advanced evolution is the rhyolite-basaltic formation in Ural.

The series of genetic types of pyritic deposits culminates in the pyritic polymetallic deposits of Altai and Japan (Kuroko type), linked with products of deepest differentiation of magmatic chambers and formation of a great volume of acid magmas.

Perimetalliferous metasomatism in pyritic deposits, on the whole uniform enough, brings about formation of quartz-hydromica perimetalliferous rocks. A typical zoning of metasomatites is indicated on fig.9.2 for pyritic deposits of the Kuroko type in Japan. In the zone of a channel of solution transfer takes position the most altered silicified rocks with dissemination of pyrite and chalcopyrite. They are surrounded by a zone of quartz-hydromica alteration with finely

disseminated pyrite, and still farther from the channel takes position argillized rocks, composed of quartz, of mixed minerals of the mica-smectite and chlorite type. These rocks gradually pass to slightly altered enclosing rhyolites. Pyritic deposit is directly bordered by a thin little zone of magnesian chlorite; at the periphery of the pyritic lens are displayed trains of thin-grained silico-hematite rocks. Amongst rare minerals present in ores of Kuroko type [Geology of Kuroko deposits, 1974], are recorded pyrophyllites, associated with diasporite in the fine-grained black (polymetallic) ore, and kaolinite. Non-metalliferous minerals in the ore bodies are gypsum and anhydrite, underlying a pyrite deposit, and barite situated in a body merged with sulfides of black ore. On data of isotope analysis of oxygen and hydrogen in metasomatic minerals, the isotope composition of the water of the solution which has produced metasomatism tallies with the composition of oceanic water with small admixture of magmatic one. In the composition of ore minerals is found the presence of magmatogene elements arising from the depth. So, in sphalerite is contained an increased content of bismuth, cobalt and nickel, in galenite antimony, arsenic and mercury, in pyrite bismuth, nickel and cobalt. These elements are not characteristic of enclosing rocks and may come either from deep seated chambers with ultra-basic and basic melts (nickel, cobalt), or from transmagmatic fluids born in the mantle (mercury, arsenic, antimony).

In pyrito-polymetallic deposits of Altai type linked with sodico-potassic magmatism, sericite metasomatites have a substantially potassic composition. From the deposits of Kuroko type considered above differs the mineral composition of these metasomatites by the presence of carbonates (calcite and breunnerite) which coincide with the inner zone of perimetalliferous alteration. Such perimetalliferous metasomatites are in mineralogical composition analogous to beresites. V.B.Tchekvaidze [1981] propounds the following lateral matasomatic zoning for the Tichono deposits from enclosing rocks to the axial part of underore products of acid metasomatism: slightly altered porphyrite, sericite + quartz + chlorite + calcite (+ pyrite + rutile), sericite + quartz + breunnerite (+ pyrite + rutile), sericite + quartz (+ pyrite + rutile). Probably the development of carbonates in this type of deposit is linked with the sufficient depth of their formations in regional shear zones and, consequently, with increasing fugacity of CO₂ in the fluid. This permits to suppose a closer link of formation of the given deposits with the manifestation of magmatism. There are even data on participation of sulfide melts in ore formation [Starostin et al., 1979]. The small role of sea-water, relatively to endogene, in ore formation is here confirmed by data on the composition of a hydrothermal solution based on the study of fluids enclosed in ores: the quantitative correlation of cations in the solution (Mg > K > Na) differs from that in sea-water (Na > Mg > K).

In the Ural type periore metasomatites are subject to regional metamorphism and represent a quartz-sericite-chlorite facies, in which are

distinguished rocks substantially silicated with pyrite, or quartz-sericitic with pyrite, quartz-sericite-chlorite and quartz-sericite-chlorite-albite rocks transient to enclosing porphyrites. Moreover, there exist essentially sericite and chlorite rocks directly contiguous to massive-sulfide ores. Amongst uncharacteristic minerals are noted paragonite, datolite and turmaline, and amongst rare ones pyrophyllite, diaspore, corundum, andalusite, and in non-metamorphosed deposits mixed-layered minerals of the mica-smectite type. Mentioned aluminium minerals are described in the altered rocks of the Kaban ore field in Central Ural [Loguinov, 1945] near contacts with granitoid massifs. Minerals of boron are found in small quantity in silicified rocks. Basically that is turmaline, but in some deposits in south Ural are found veins of pink datolite. Particularly interesting are the occurrences of paragonite. Formerly this mineral was found in shales and counted as product of regional metamorphism, as opposed to potassium mica of periorite altered rocks. Data have appeared about the content of a sodium component in periorite sericites [Loguinov *et al.*, 1976], but they also were linked with the superposition of regional metamorphism. However, the works of A.I.Grabezhev showed the link of paragonite formation in quartz-sericite rock with ore emplacement [Grabezhev *et al.*, 1995]. The appearance of sodium metasomatism, telescoping acid alteration, serves as confirmation of the existence of sodium saline melts, metals extracted from the magma and then taking root behind a mobile acid solution in enclosing vulcanites. According to A.I.Grabezhev, the sodium character of metasomatism with formation of paragonite is inherited from the substantially sodic type of the siluro-devonian magmatism in central Ural.

In small quantity is found chrome-containing potassic mica, fuchsite, in periorite quartz-sericite rocks. Its occurrences attest to addition in the zone of pyrite formation, at least of part of elements from a deep source, since immediately in the context of pyrite deposits are absent ultra-basic rocks that could have been sources of chrome.

So, the composition of metasomatic periorite rocks on pyrite deposits distinctly reflects dependence upon the character of magmatism, signs of activity of deep fluids and correlation with the composition of ores. The supplied material corroborates the fundamental position of the hypothesis propounded above of an “ore saline melt”, separating at a determined stage of evolution of the magma under influence of transmigmatic fluids.

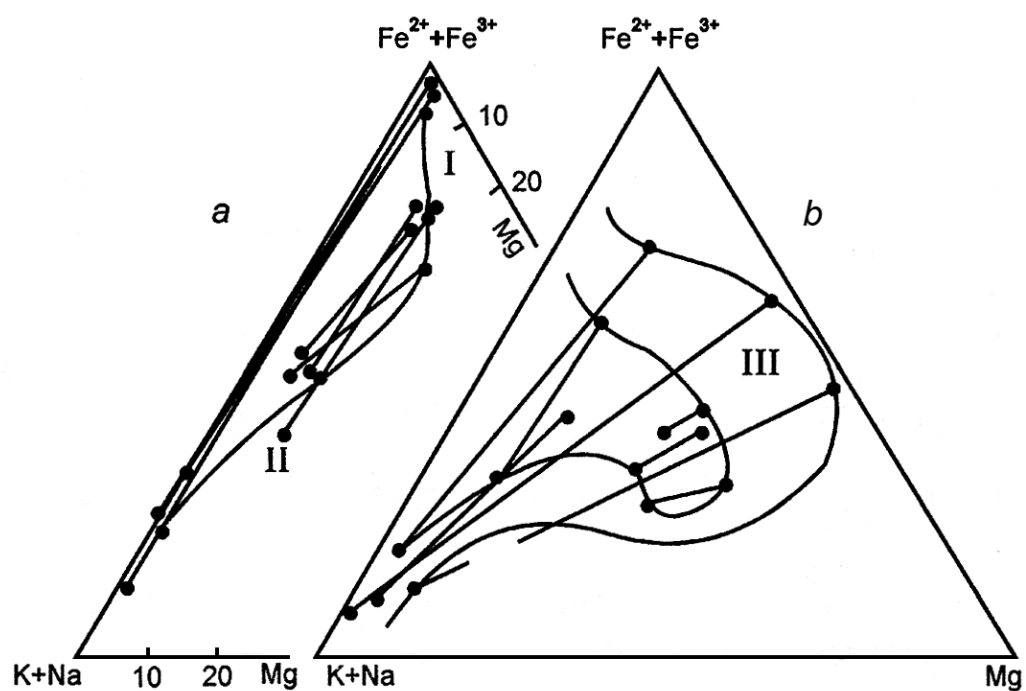


Fig. 9.1 Liquidus diagram of differentiation of residual ferruginous liquids in regime of low (a) or high (b) fluid pressure.

I - ferrobasalts; II - ferroandesites (islandites) and ferro-rhyolites; III - basalts; IV - andesites and rhyolites.

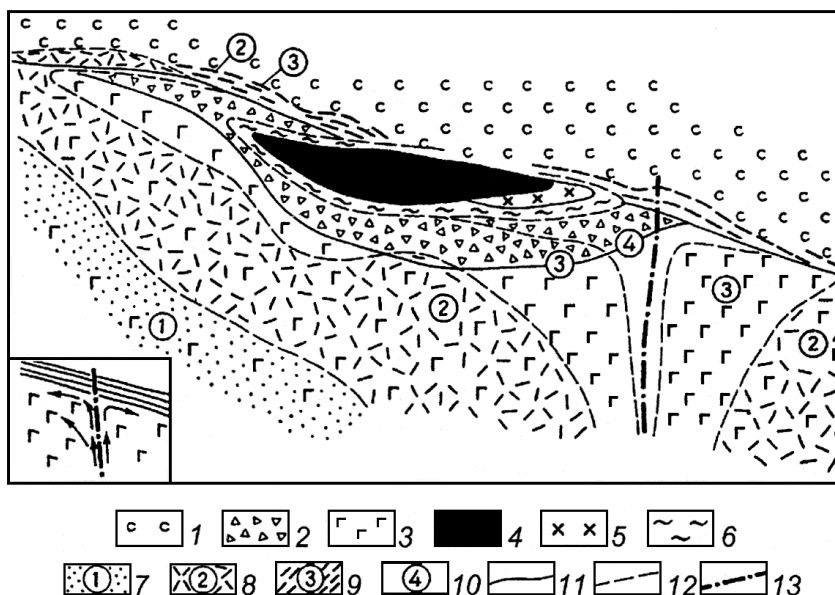


Fig. 9.2 Scheme of metasomatic zoning (vertical section) in perire altered rocks of Kuroko deposits. In lower left corner is indicated the presumed direction of the solutions [Zotov & Rusinov, 1975]

1 - argillites; 2 - breccia and rhyolitic tuffs; 3 - “white” rhyolites; 4 - massive sulfides; 5 - gypsum; 6 - chloritic rocks; 7-10 products of perire metasomatism (digits in parenthesis designate number of zones); - 7 propylitized rhyolites; 8 - argillized rocks; 9 – quartz-hydromica rocks; 10 - quartz-pyrite rocks; 11 - lithological limits; 12 - limits of metasomatic zones; 13 - fracture.

CHAPTER 10

Magmatism, metasomatism and rare metal mineralization

Ores of tungsten and molybdenum are in general associated with silicification and feldspar metasomatism. Tungsten deposits are linked with granitoid magmatism and situated either directly in apical greisenized granitic cupolas, or in skarns with superimposed greisens. Tungsteniferous granites are characterized by an increase in iron and alumina and by fluor content and belong to the reducing type [Abramov & Borizovski, 1996], i.e. crystallize at diminished oxygen fugacity. These composition peculiarities of tungsteniferous granites witness to the notable reciprocal action of fluid and magma in course of evolution of the magma in conditions of open system (i.e. in a flow of transmagmatic fluids). The action of fluids on crystallisation of granitoid melts is attested by the high degree of microclinization and albitization of granites (cf. fig. 7.3). In ascending direction, immutable granites are replaced by microclinized, and even higher, by albitized ones. Starting from this zone of albitization is observed a diffused rock greisenization, increasing upwards, to the roof of the massif. A characteristic peculiarity of such massifs is the repetition under albitized granites of a zone of microclinization, but under it, again of a zone of albitization already directly in endocontact. Greisens with tungsten mineralization coincide with this upper zone of albitisation, but quartz-tungsten veins are also situated in rocks of the massif's roof. The periodicity (rythmicality) of structure of tungsten granite massifs is reflected not only in the zoning of feldspars. In the apical part of such massifs are observed areas of development of rhythmic-banded quartz-granites. An example of such situation has been described in granites of Central Kazakhstan (Povilaitis, 1966). Tungsten-containing granite massifs with greisens are usually surrounded with slightly keratinized enclosing rocks; moreover, intense greisenization and maximal increase in tungsten content coincide with endocontact in apical part of the massif. This shows that the apical part of the massif of crystallizing granite

was sealed above by slightly permeable enclosing rocks, usually shales, i.e. itself constituting a relatively closed system, a snare for the rising magmatogeneous fluids.

Interpreting interrelations between magmatic (silicatic) melts, metasomatism and tungsten mineralization is possible on the basis of experimental phase diagrams correspondence (cf. fig. 6.2). Lower arrows indicate trends of homodromous change of composition of the melts, conditioned by their crystallization differentiation. On all the extensive change of composition of the melts it is possible for hydrothermal solutions to separate from them; these solutions, judging from experimental data, cannot effectively concentrate metals in themselves: their tungsten content is at the same level as in the silicate melt from which they separate. A strong ore-concentration effect in the studied systems is only attained with development in them of melt heterogeneity, reflected in the separation of fluid salt-rich phases (III, IV, V on fig.6.2), where tungsten concentration may increase in one order of magnitude compared with the melt. This effect determines the capacity of magmatic systems to generate ores. This is linked to the degree of salt accumulation in the track of magma heterogenizations, which requires a relative closing of the system, so that transmagnetic fluids cannot wash away salt components.

An important peculiarity of salt ore concentration is its selectivity, which determines the metallic composition of ore deposits. For instance, tin is indifferent to relation with fluorids, which effectively extract tungsten, and tin concentration in fluoridic salt melts does not exceed its concentration in a hydrothermal solution. As tin concentrators serve chloride melts. It is interesting that in fluoride melts, extremely poor in silica, alumina content in all the studied systems (except these of granitic –LiF) remains high, close to its content in the initial melt. This circumstance has been used in elaborating a liquation method of extracting aluminium from non-bauxitic raw materials [Marakushev et al., 1991]. By varying the salt composition it is possible to obtain another tendency and modelise in magmatic systems processes that lead to simultaneous accumulation of silica and metals, which finally culminates in the formation of quartz-ore veins. The composition of these melts may be reduced to two components: an alkaline silicate (Na_2SiO_3 , Na_4SiO_4 etc.) and ore salt (MF_n , MCl_n etc.), which in lowering temperature may react reciprocally and form quartzitic ore phases ($\text{M} + \text{SiO}_2$) and mobile halogenides, easily dissolved, of alkaline metals: $1.5\text{Na}_2\text{SiO}_3 + \text{MF}_n = \text{M} + 1.5\text{SiO}_2 + (n\text{NaF})$. In the same way can be formed quartz nuclei in granite pegmatites and ore veins, whose transportation accompanies separation of hydrothermal solutions that brings about periere metasomatism. As confirmation of the reality of the propounded sketch is displayed the detection, included in minerals of quartz-ore veins, of fluids, not only of low density and low salinity, but also of highly dense solutions with concentrations up to 20-30 and even 45% equ. NaCl.

Granitic magmatism develops under the influence of flows of transmigmatic fluids. Enormous masses of precambrian granites are formed in conditions of an open system and flows of fluids wash away from the melt a salt load, depositing it outside the limits of the system. That is why such granite masses are oreless. A similar situation prevails in deep and in average horizons of more recent granite batholiths formed at depths in the order of 5-10 km. The fluid crosses these areas, encountering no obstacles. In the upper part of the batholith fluids accumulate in structural tracks of granite apophyses in the roof and assists salt accumulation. Under the screen, fluid pressure increases, the vertical gradient of pressure diminishes, serving as motive power for the ascending fluid. As a result, after a lapse of time, the flow of fluids slows down, and suddenly begin the cooling down of the melt, its crystallisation and heterogeneization. The forming heterophasic hydrothermal solutions penetrate through cracks into the surrounding rocks and differentiate themselves into hydrothermal low density solution and dense viscous salt-ore phase. The solution rises in front, as more mobile phase, and brings about metasomatism, but the salt part moves more slowly, penetrates later and deposits ore. If conditions are not favourable to differentiation, phase separation does not occur, and metasomatites are formed with a disseminated mineralization.

CHAPTER 11

Boron metasomatism, sodium metasomatism and gold mineralization

In the geological literature about ore bodies in gold, tin and some other deposits mention is more than once made of metasomatic albitization. Its appearance is linked with the sodic character of solutions transferring and depositing gold and tin, and with decomposition of sodium-containing soluble complexes of these metals. In these same deposits is carried out a development of dispersed turmalinization accumulated in veinlets, which basically coincide with on-ore or above-ore horizons. Turmalinization's relative time is estimated by various authors rather differently, from preore to synore. Research on metasomatism and gold-ore veins and black shales deposits have shown that both turmalinization, as well as, albitization in different quantitative correlations are present in all these deposits. This might mean that both manifestations result from one and the same process, the action of one and the same solution with high activity of sodium and bore. However, with these suppositions do not accord the opposite acido-basic characters of these elements. Moreover, metasomatic turmaline and albite principally concentrate on different depth levels of deposits or ore bodies and reveal signs of non-simultaneity. Turmalin is observed in association with quartz, more rarely with sericite and pyrite, in acid preore metasomatites in upper parts of deposits. Metasomatic albite displays veinlets around ore bodies or inside them on average and deep horizons, but in the course of time, it precipitates near the main ore associations or simultaneously with them. In some places the albite veinlets themselves are auriferous. Truly, albite and turmaline are not always spatially separate. For instance, in ore field Muruntau in some parts of drill core MC-3, depth intervals of turmalinization and albitization overlap and turmalin veinlets are surrounded by fringes of metasomatic albite. In other parts of the core of the same drill, turmalin and albite are observed separate (fig.11.1); moreover, albitization coincides with ore intervals, but zones of the most intensive turmalinization are displayed upwards. On the Sovietskoie deposit turmalinization is seen over

separate ore bodies. Over the upper ore bodies it is seen in the quarry, but in the deep shaft horizons it is fixed over the other ore bodies. Similar correlations are typical and are repeated in big streaks on many auriferous deposits.

In some deposits of epithermal and porphyric type tourmaline is concentrated in bodies of explosive breccias, which are formed with outbursts, produced by massive degassing emission of magmatic melts. This witnesses concentration of boron together with other volatile components in the residual magmatic melts. About links of boron with other volatile components, in particular with fluorine is corroborated with the increased content of the last in the composition of tourmaline of some of the investigated deposits. For example, in tourmaline from the Muruntau ore-field is contained up to 0.72% fluorine.

The geochemical link of sodium and boron in a hydrothermal process is distinctly evidenced by analysis of data on the composition of waters in geothermal areas of active volcanism. On a diagram constructed upon data of A.G.Ellis [1987] (fig.11.2), is visible the straight interdependence between the contents of these elements in thermal waters. In the same work is propounded, as results of drilling in geothermal areas, the composition of deep “initial” thermal waters and waters arising from bore-hole. Deep waters are substantially impoverished in boron and sodium, compared with the latter, which shows the differentiation and, possibly, stratification of solutions in the bore-hole at sinking of pressure and temperature with upwards withdrawal of a less dense phase, enriched with volatile matters, in particular with boron. In this way, analysis of natural manifestations of tourmalinization in ore fields and of boron content in volcanic hydrotherms reveals a rather close link of boron and sodium, but at the same time also shows a difference in their behaviour, occurring at a determined stage of the solution’s evolution.

Concerning the source of boron in hydrothermal deposits there exist two opinions: 1) supply from a magmatic deep source and 2) redeposition with extraction from enclosing rocks. On the majority of deposits are visible aureoles of boron diffusion, but no aureole of impoverishing (removal), therefore there is no reason to suppose boron to have been borrowed directly in periorite metasomatism of enclosing rocks. Tourmaline in those aureoles has an increased fluorine content, a characteristic component of remaining deeply differentiated granitic melts and of fluids accompanying them, but in parallel with tourmalinization there occurs sodic metasomatism in the form of albitization. Comparison of these facts permits to suppose that in ore deposits boron basically has come from magmatic fluids. Boron may fall into magma with different properties: it may come from deep transmagmatic fluids or be borrowed from a melt at the magmatic replacement of basement rocks. It is important to notice that the main mass of boron in metasomatic ore fields has been brought by a magmatic fluid.

At cooling down and subliquidus crystallization of the granitoid magma, the residual melt gets enriched in silica, alkalis and volatile components. Boron, having a small ionic radius, near that of aluminum, isomorphically replaces aluminum in the structure of the aluminosilicated melt and stays in the remaining melt together with fluorine, whereas the other volatile components, for instance chlorine, are distributed in fluid phase upon earlier stages of crystallization. Increasing content of boron in the melt changes granite eutectic toward albite (quartz + albite + potassic feldspar) enriched in sodium. In the subliquidus area in the $\text{H}_2\text{O}-\text{NaCl}-\text{NaAlSi}_3\text{O}_8$ system, there may exist silicate and salt melts, and fluid. Moreover, sodium accumulated in eutectic melt is accompanied by an increase of sodium content also in the coexisting salt melt. At the final stage of magma crystallization boron separates from the melt owing to crystallization of a significant part of the latter and thus, concluding portions of the salt phase are enriched in sodium and boron. At sinking pressure and temperature, insofar as this phase nears the surface, the fluid phase separates from it, its volume increases and has its volatile components easily redistributed, amongst them boron, while sodium remains in salt phase. The salt phase, concentrating in itself ore components and sodium enrichment, is hardly mobile and stays, but while moving to the surface from an easily mobile fluid phase, having an anionic composition and being enriched, notably in boron. The salt phase, according to the statements of A.A. Marakushev, deposits ore mineralization, while the fluid phase brings about preore acid metasomatism, including turmalinization. In this way, sodium and bore, closely linked with the silicate and salt melts, separate at the splitting of the salt phase with secretion of acid fluid.

Turmalinization does not always occur intensively; sometimes turmaline is found in metasomatites in the form of accessory mineral. Apparently the degree of development of turmalinization is determined not so much by the quantity of bore in the magmatogene fluid as by the conditions of its precipitation. For turmalinization it is advantageous, in order for acid metasomatism to occur at high temperature, to have a relatively earlier stage of evolution of a hydrothermal solution, such as takes place in copper-molybdenum-porphyries, boron-bearing silicates skarn deposits and gold-quartzitic deposits in black shales. But if acid metasomatism shifts to a low temperature area, turmalinization occurs feebly. In these conditions magnesium and aluminium associate in micaceous silicates (chlorites and clayey minerals), while boron remains in the solution and is disseminated. Such a situation is characteristic of some epithermal gold-silver deposits that are accompanied with periore argilization, and gold-sulfidic deposits, included in black-shales series.

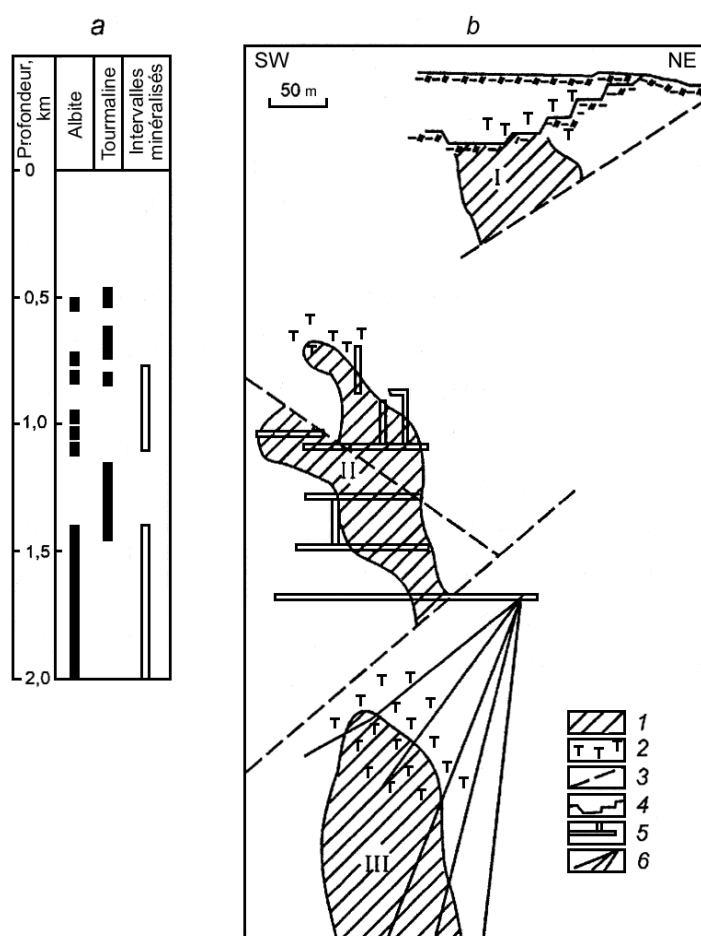


Fig. 11.1. Relations of zones of albitization and tourmalinization of gold ore deposits.

a - extension of albite, tourmaline and ore intervals in core of well MC-5 (ore field Muruntau, West Uzbekistan); *b* - position of tourmaline zones in a vertical section through Soviet deposit. On plane section of ore zones II and III projected from ore zone of Quarry area (I). 1 - ore zones; 2 - aureoles of tourmalinization; 3 - dislocation faults; 4 - quarry benches (schematically shown); 5 - subterranean galleries; 6 - bore holes.

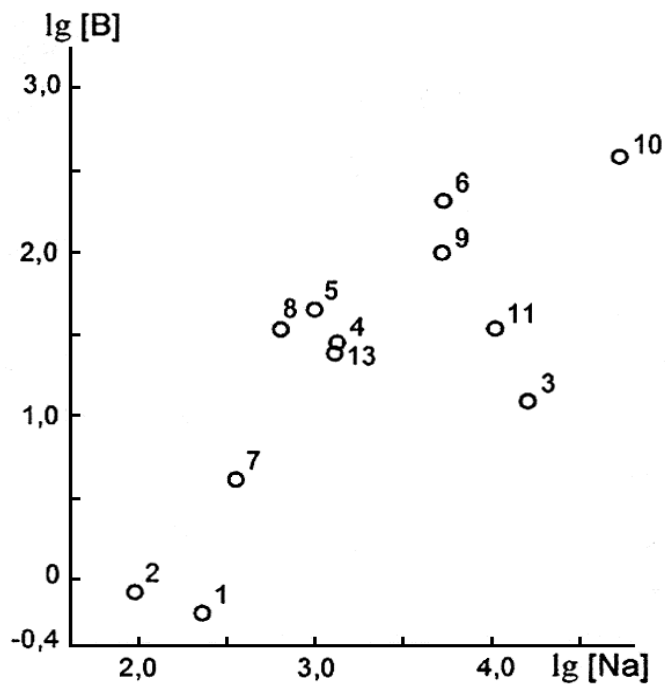


Fig. 11.2. Relations between sodium and bore in waters of hydrothermal bore holes of the world.

Digits of points indicate geothermal fields and their bore holes [Ellis, 1982].

CHAPTER 12

Metasomatism and epithermal gold-silver mineralization

The avalanche of researches and publications, in the middle of the 20th century, about periorite metasomatism has, in the seventies, abated, due to a certain disappointment in the effectiveness of these researches. The greatest difficulties were clarified in the discrimination of ore-containing metasomatites from the general mass, in which predominate, as to volume, oreless varieties. Moreover, the mechanism was not studied, linked with ore deposits and periorite alteration of enclosing rocks, but that provoked uncertainty of the geologist in applying empirically observed rules to search and prospecting. D.S. Korzhinsky's statement about "forestalling wave of acid components" in precipitating ores after stages of acid metasomatism in late alkali stage had a purely general, not sufficiently concrete character. In many cases, other factors exert a predominating influence on ore precipitation: temperature, fugacity of oxygen, sulphur, etc.

A new impulsion to research of periorite metasomatites came from the appearance in the nineties of publications on epithermal gold metasomatites, taking into account the latest data on isotopic composition of oxygen, hydrogen and sulphur of hydrothermal fluids, either metalliferous or metasomatizing, as well as data on cation-anion composition of solutions, their oxydo-reducing, acido-basic properties [White and Hedenquist, 1995]. In these and other works was shown the possibility not only of distinguishing oreless metasomatites from ore-bearing, but also of determining, after the character of periorite metasomatism, the type of ore mineralization for a given field of deposits.

Epithermal deposits are formed at small depth of the order of 1-2 km at a temperature of 150-300°C with active participation of underground waters of meteoric origin. That is why conditions of hydrothermal activity are in a large measure determined by the paleogeographic and hydrogeological situation of the region. The dependence upon these conditions of periorite metasomatism and the

character of mineralization for massive sulfide type of deposits formed in submarine volcanic series on one side and subaerial ones on the other has been discussed by V.P. Loginov [1970]. Differences have been evidenced between the two mentioned groups of sulfide ores. They are included in a high development of albite, kaolinite and intense silicification (up to formation of quartzites with diaspore and andalusite) in the “subaerial” type and significantly lesser acidity and oxidation of the solutions formed in the “submarine” type of deposits, in which the enclosing rocks have turned up preferentially sericitized. Recently a similar distinction has been extended to epithermal gold-silver deposits, formed in conditions of different aeration of underground waters [Rusinov and Rusinova, 1977]. Only, these observations were not clearly enough linked with differences in ore mineralization. It was only possible to show that in the “subaerial” type are found faded ores with a high degree of oxidation of tellurium (goldfieldite).

The first two types of epithermal mineralizations, differing in character from periorite metasomatism, were divided into adular-sericitic and acido-sulfatic types [Heald et al., 1987]. Recent studies of ore mineralogy, of physico-chemical environment of ore deposits and isotopic light elements studies have led N.K. White and J.W. Hedenquist to precise and more fully formulate the principal differences between these types of deposits, which were given the names of low sulfidation (corresponding to adular-sericite) and high sulfidation (corresponding to acid-sulfate) [White and Hedenquist, 1995]. The term high sulfidation signifies that in ores of a given type participate parageneses of sulfides with high oxidized states of metals (As^{5+} , Sb^{5+} , Te^{4+} , Cu^{2+}), for instance enargite, luzonite, goldfieldite. In connection with high valence of the metal, the sulfur/metal relation in these minerals is also high. On contrary, in the ores of low sulfidation the metals' valence is lowered (As^{+} , Sb^{3+} , Te^{2+} , Cu^{+}) and the sulphur/metal relation in the corresponding minerals is low. Both treated types of deposit are formed from fluids differing in chemical composition. The depositing fluids of the low sulfidation type are analogous to hydrothermal springs in the bore-holes on contemporary geothermal fields. They have an acidity index near neutral and a relatively reducing character. High sulfidation systems are associated with acid fluids formed in magmatic-hydrothermal environment [White and Hedenquist, 1995] and having an oxydizing character.

Isotope researches have shown that in the environment of low sulfidation in thermal springs predominates meteoric water, although presence of magmatic water and magmatic gases (CO_2 , SO_2 , HCl) is also encountered [Hedenquist and Lowenstern, 1994]. Fluids of this type in depth, in area of origin, were in equilibrium with the enclosing rocks and therefore had the character of neutral reducing hydrotherms, in which CO_2 , H_2S and NaCl had important soluble forms. On fluid arrival in regions of small depth and low pressure it emits a gaseous phase, enriched in CO_2 and H_2S . Gas condenses on the surface in

subsoil waters; with that, H₂S oxydates at the expense of atmospheric oxygen, and there arise, steam heated, ultra-acid sulfate waters with pH = 2 – 3 at T = 100°C. Accordingly, in the zone of H₂S oxidation arises an intense acid metasomatism with silicification of the rocks and removal of all or nearly all components, except silica and, partly, alumina. Gently pitching layers are formed, or lenses of monoquartzites, quartzites with alunite and kaolinite, which abruptly give way under quartz-sericite-adular metasomatites, forming steeply

Characteristic properties.	Types of deposit	
	Highsulfidation	Lowsulfidation
Form of ore bodies	Predominate: zones of dissemination and metasomatic bodies	Predominate: veins and stockwerk zones
Vein minerals	Quartz, barite	
	kaolinite, pyrophyllite, diaspore, alunite	adular, illite, sericite, calcite, calcic edonite
Ore minerals	Pyrite, sphalerite, galenite, chalcopyrite, tetraedrite-tennantite	
	Enargite, luzonite, covellite	Arsenopyrite, electrum, tellurides, selenides
Examples of deposits	Goldfield(USA), Summitville(USA), El(Chile), Rodalquilar(Spain), Lepanto(Philippine)	Emperor(Fiji), Golden Cross(New Zealand), Porgera(New Zealand), Round Mountain(USA), Karamken(Russia)

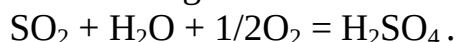
Table 12.1. Comparative description of low sulphidized and highsulphidized epithermal deposits after [White and Hedenquist, 1995]

pitching zones. Precisely in the axial parts of such zones of metasomatism, occurring in slightly acid milieu, are distributed ore bodies. That is why detection of metasomatic zoning has significance for determining the position of flow of fluids and, consequently, most probably that of ore mineralization. Comparison of the environment of these two types is offered on fig.12.1 and table 12.1.

Using the analogy of the described ore system with contemporary active geothermal systems, in which are directly measured temperatures of formation of mineral parageneses of altered rocks, it is possible to follow paleo-isotherms in ore systems along parageneses of metasomatic minerals. Determining the

position of paleo-isotherms is important for evaluating the level of erosion level of the epithermal system. Most epithermal ores are deposited in temperatures of 180 to 200°C, which implies a depth of 100 to 800-1500 m below the paleo-level of underground waters [Hedenquist and Henley, 1985]. If in the discovered ore manifestation a mineral formation occurs at a temperature above 200-250°C, this means that the system is deeply eroded and therefore of small interest as ore object. A low temperature of mineralization indicates weak erosion of mineralization and possibility of ore detection in depth. The cited authors give as good indicators of paleotemperatures clay minerals with variable inter-layered spaces. With rising temperature smectite (whose stability in hydrothermal natural conditions is limited to a temperature below 160°C) is transformed into illite-smectite and even illite, which is stable at a temperature over 220°C [Reyes, 1991]. Precisely such a succession is proper to periveinous metasomatites insofar as nearing the ore vein in epithermal gold-silver deposits, such as, for instance, Baleiskoie (Transbaikal), Karamken (N.E.Russia). Ore veins contain adular and calcite, indicating less acid condition of ore formation than in periveinous metasomatism. To temperature sensitive minerals are related zeolites (T more than 200-220°C), epidote (more than 200-240°C), and also, at even higher temperature, biotite and amphiboles, depositing in root parts of the epithermal mineralisation.

In an environment of high sulfidation, fluids separate from a relatively oxidized magmatic source [White and Hedenquist, 1995] and rise, slightly reacting with enclosing rocks. Gases arising in the fluid composition may get absorbed in underground waters with dismutation of sulfide gas:



As a result there arise ultra-acid (pH=0-2), hot (200-300°C) oxidizing solutions which, reacting with enclosing rocks, bring about acid metasomatism with silicification and removal of most of the rock's components. Presence of hydrogen sulfide together with H₂SO₄ assists simultaneous precipitation of sulfide metals in the form of dissemination and a set of thin veinlets. An ultra-acid milieu of mineralization is reflected in the formation of such minerals as kaolinite, alunite, pyrophyllite, diaspore etc. Some of these minerals, moreover, are sensitive to temperature. For instance the stability field of pyrophyllite in the presence of quartz is higher than 320-360°C, but that of zunyite and topaz is higher than 260°C [Reyes, 1990]. In foreign literature the associations of enumerated minerals are related to "advanced argillic alteration", but in Russian literature, to associations of secondary quartz. In these associations, i.e. in the most acid metasomatites, are situated the zones of mineralization. This constitutes yet another difference from the adular-sericite type, in which ore mineralization coincides with the less acid metasomatites.

An essential moment in the comparison of the separate types of ore is that alunite quartzite may be present in both, but they have moreover a different

nature: in the low sulfidation (adular-sericite) type they form in the zone of hydrogen sulfur oxidation by superficial waters; but in the high sulfidation type (acido-sulfate) they form directly in the zone of ore precipitation at a depth not inferior to 0,5-1 km. It is therefore important to distinguish acid metasomatites occurring 1) in a hydrothermal process the acidity of which is conditioned by magmatic gases, 2) in superficial formation of acido-sulfatic waters, steam heated, 3) in posthydrothermal weathering of sulfide minerals.

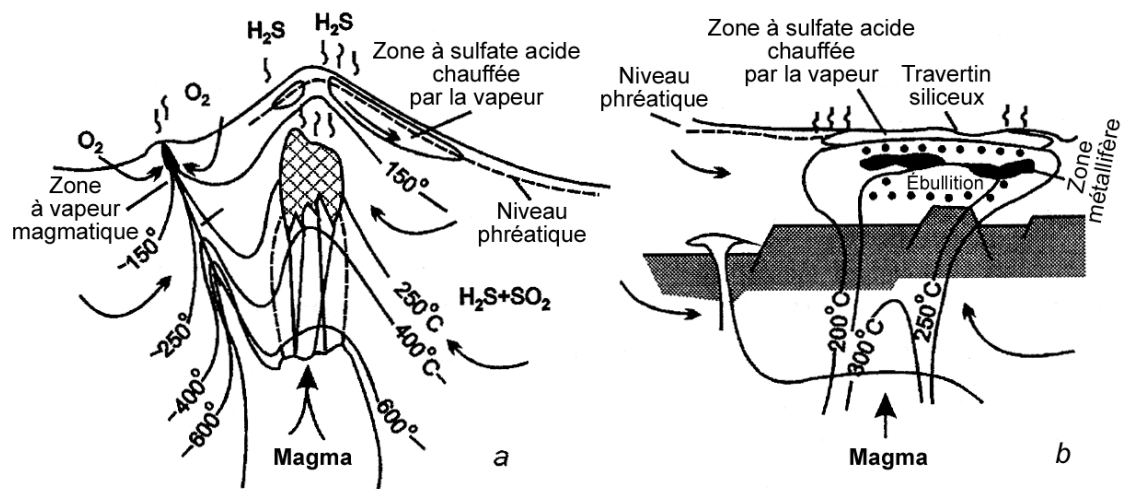


Fig.12.1. Schema showing the difference between “high”- and “low” sulfidation situations of epithermal gold deposits after [White & Hedenquist, 1995].

Part III

FORMATIONS OF METASOMATIC ROCKS

Chapter 13

Classification of metasomatic rocks

The study of natural objects convincingly shows that the existing metalliferous deposits are in close spatial connection with the different types of metasomatic formations, with which they are variously related in age and genesis. Survey of metasomatites and their utilization for metallogenic previsions requires that all their variety be characterized by positing rigorously classified categories. This implies a corresponding classification of the metasomatic rocks.

Such a classification may be accepted and successfully utilized if it objectively reflects the rocks observed in nature and if precise criteria have been elaborated allowing to place any rock, according to observed facts, into the classification. Classifying metasomatites is a more complex problem than classifying other types of rocks. For instance the magmatic rocks composition is roughly determined by that of magmatic baths and their structure by the latter condition of crystallisation. It is therefore in order to determine a magmatic rock, to know its composition and its structure. Idem for sedimentary and metamorphic rocks. But in the case of a metasomatic rock it is quite insufficient to know its composition and its structure, because these depend upon the simultaneous influence of the substituted rocks, of the degree of thoroughness of their metasomatism and the properties of the solutions. Identical solutions arouse a complex of metasomatites spatially and genetically linked, differing in

composition and structure and which for cartography it is necessary nonetheless to unite. On the other hand, owing to various hydrothermal and metasomatic processes characterized by a distinct mineral specialization, there may form metasomatites of similar composition and structure that must however be in the cartography distinguished. In correctly determining metasomatites the criteria characterizing petrogenetic processes as a whole and chiefly the solutions properties are of fundamental importance.

State of the art. The first approaches to a classification of metasomatites result in dividing them according to the character of the neoformed mineral [Lindgren, 1901, 1918, 1934-1935; Schwartz, 1939] or according to the composition of the added chemical element [Goldschmidt, 1933; Eskola, 1920; Barth, Correw et Eskola, 1939; Turner, 1951]. In the fifties the works of D.S. Korzhinski [1953], N.I. Nakovnik [1954], V.A. Zharikov [1956, 1959] outline a "formation" approach to the study and systematics of metasomatites. A "formation" significance was attributed to the terms *skarns*, *greisens*, *beresites*, *propylites*, *secondary quartzites*. Each term designated rocks linked to a rigorously defined petrogenetic process. So, N.I. Nakovnik [1954] considered secondary quartzites as a genetic, independant complex of enclosing metalliferous rocks, characterized by typical geological, petrographic, mineralogical and metalliferous tokens. The necessity of a "formation" approach of the systematics of metasomatic processes was for the first time scientifically discussed by V.A. Zharikov in 1956. He showed that the designations used with reference to a newly formed mineral or an added chemical element are unsuitable for classifying metasomatites because the entirety of the various mineral and chemical modifications synchronically occuring in the various parts of the geological body exposed to the influence of hydrothermal solutions prove to be the essential feature of practically all metasomatic processes. Attempts to a more thorough "formation" approach of the classification and cartography of metasomatites were made by V.A. Zharikov et B.I. Omelianenko [1965, 1966, 1978, 1992], D.V. Rundqvist & I.G.Pavlova[1974], G.M.Belyaev and V.A.Rudnik [1978], Ye.V.Plyushchev [1978], A.Ye.Shlygine and V.D.Gukova [1981], V.V. Zhdanov [1983], O.N. Gryaznov [1992]. The development of the "formation" approach has been greatly influenced by the works of the six USSR colloquies on perimetalliferous metasomatism in Leningrad from 1963 to 1987, as weel as of the regional colloquies on the problem, especially about Ural metasomatites. At present, the "formation" approach is adopted by all the specialists in the CIS. At the same time, many disagreements have arisen about the terms *metasomatic formations* and *metasomatic facies*, applied to different types of metasomatites, to the nature of the link between metasomatites and magmatic, particularly metamorphic processes, and the mutual relation of the different types of metasomatites. Various approches have been made to

cartography metasomatic rocks and the use of its results for the search for deposits. Many difficulties arise from the lack of a unique principle of designation, cf. infra.

General features of metasomatic formations. The classification succinctly and schematically reflects the main features of metasomatites. It is based on several positions summarizing the study of metasomatic phenomena :

- under the action of solutions of such and such genetic type occur various metasomatic rocks of which structure and composition are determined by the solutions' properties, the composition and structure of the initial rocks and the latters' degree of metamorphic transformation;
- any metasomatic body formed by the action of hydrothermal solutions of a determined genetic type has a zonal structure characterized either as a metasomatic column (if the metasomatic body is formed in homogeneous surrounding) or metasomatic columns (in heterogeneous surrounding);
- composition of an internal (rear) zone characterizes a condition of equilibrium attained between the rock and the initial solution and is roughly determined by the solution's properties;
- composition of an external (front) zone characterizes a condition of equilibrium attained between the rock and the exhausted solution and is roughly determined by the composition of the rock submitted to a substitution;
- in any process of hydrothermal metasomatism can be distinguished on one side an early stage of rocks metasomatism, on the other terminal stages in which are formed veins, cement of breaches and associated periveinous modifications superposed on the metasomatites formed earlier on;
- rock transformations which are the most significant as to size and determine the main typomorphic characters of metasomatites are linked to the early stage of hydrothermal metasomatism;
- at the terminal stages the properties of the hydrothermal solutions are altered, hence the development within the metasomatic body of later mineral associations superposed to earlier formed;
- contrary to early stage metasomatism which occur on a continuous front, those of the latter stages occur sporadically, tending to weigh upon veins and fissility zones, complicating and somehow masking the metasomatic aureoles of the early stage;
- apart from rare exceptions, metalliferous mineralization occurs at the terminal stages of the processes of hydrothermal metasomatism;
- the terms used in classifying metasomatic rocks always refer to the early stage; the others are characterized by a complementary term (for instance, beresite with ensuing chloritization);
- five sorts of minerals contribute to the composition of metasomatites :

- a) minerals formed at the early stage of hydrothermal metasomatism;
- b) minerals of the initial rock remaining stable during metasomatism;
- c) residual, non entirely substituted minerals which despite their stability during metasomatism, but owing to causes preventing completion of metasomatic reactions, have been kept in the metasomatized rocks;
- d) minerals formed in the terminal stages and developing to the detriment of earlier formed;
- e) minerals contributing to the composition of veins, cement of breaches, that have formed owing to filling up of free cavities.

Many points universally admitted only concern particular types of metasomatism. No doubt has been uttered about the genetic link between some of them and certain magmatic formations. However, such a link is difficult to prove for other types of metasomatic rocks. We are far from having established for all types of metasomatites, mutual relations in age and genesis. And this is what makes open to criticism classifications made about the metasomatites belonging to which types of magmatic rocks and which stages of the hydrothermal process [Zharikov, 1956, 1966; Zharikov and Omelianenko, 1965, 1978]. Certainly less open to discussion is a classification in which metasomatite associations observed in nature are distributed according to acidity-basicity and temperature of the solutions [Zharikov, Omelianenko et Pertsev, 1992]. Unfortunately such a classification is more formal and does not reflect the important genetic relations already established for some types of metasomatism. This deficiency may be partly eliminated by introducing complementary features into the classification (table 13.1). This has seemed to be the most productive way to the proposed classification.

Basic principles of a classification of metasomatites. Every classification may be expressed in a succession of therms such as brick - house - quarter - city, i.e. it may contain elements relative to different levels of organization. If these elements really occur in nature and are based on the current methods in geology, such a classification may be admitted by the specialists. Concerning metasomatic rocks, such elements are the following.

- A. Zone of the metasomatic column representing a natural body formed by a fixed paragenesis of minerals in equilibrium. This zone is the singular initial term of the hierarchic scale of classification categories. Such zones may have been determined by usual methods of geology using documentation and microscopically studying thin plates.
- B. Metasomatic column (facies) representing entirety of metasomatic zones, disposed in a determined sequence and formed at the expense of rocks of a

certain composition. To the designation of each facies is associated that of the initial rock (for instance, apogranitic greisen, apocarbonatite, etc.). The columns' constitution is based on the study of thin plates taken from all over the metasomatic bodies. Although the diversity of facies is determined by the constitution of the initial rocks, these facies may also in many cases differ according to the variation of the intensif parameters (temperature, pressure, pH, Eh, chemical potentials of the perfectly mobile components) peculiar to such and such petrogenetic process. For instance there may have occurred for the propylites, according to temperature, a facies with actinolite-epidote, epidote-chlorite or chlorite-carbonate.

- C. Metasomatic family representing an entirety of metasomatic facies formed by solutions of a certain petrogenetic type. This formation is considered as a chief element of classification. Owing to its exceptional importance it will be especially explained below.
- D. The group of metasomatic formations genetically acquainted, representing metasomatites of consecutive elaboration belonging to various types of formation but to the selfsame hydrothermal cycle. Such groups are distinguished by their dependance upon the magmatism type and the latter's depth of manifestation. For instance, in connection with magmatism of an intrusive granitoid of a certain stage they may form silico-alkaline metasomatites (products of granitisation), magnesium skarns, feldspathic metasomatites, calcic skarns, greisens, constituting one group of associated metasomatic formations. For cartography of metasomatites in the vast regions in which occur various stages of magmatic elaboration, it may be useful for the metallogenic prevision to distinguish between the associated metasomatic formations. The volume of this kind of classification nearly corresponds to the "formation of regional metasomatism" of E.V. Pliushchev [1978] or to the "pneumato-hydrothermal (fluidogene) complex" of A.E. Shlyguine and V.D. Gukova [1981]. In most cases for the systematics of metasomatites at this level the data are insufficient since the maps are partly hypothetical.

Metasomatic formation as a basis of a classification of metasomatites.

Thorough investigation of formational analysis in geology has led to systematizing and coordinating many data about magmatic and sedimentary rocks and the metalliferous deposits. It is generally admitted that metallogenic analysis is fundamental for metallogeny. Since metasomatic formation is a particular case of geological formation, it must closely correspond to the fundamental meaning of this term. Opportunities to use the term formation in the study of the various geological series are given by N.S. Shatsky [1964]

definition according to which the formations are natural complexes or associations of rocks in mutually close paragenetic connection in age and space. If minerals are parageneses of elements and rocks parageneses of minerals, geological formations are parageneses of rocks. There are many other definitions of this term, betraying the objective difficulty in clearly determining the limits of a formation.

The specialists in formational analysis Y.A. Kuznetsov [1964], N.S. Shatsky [1965], N.P. Kheraskov [1967] have underscored the need to support formulation of any geological notion as elements that can be established with the usual methods of geology. Hypothetic elements should be excluded from the definition of crucial notions such as "formation". Only elements that can be observed and studied should intervene, or else every researcher will give his own interpretation depending upon those petrological hypotheses that suit him best. Admittedly, none of the formulations so far given of the notion of "geological formation" wholly meets that requisite. Although formation constitutes a group of really existing unities directly accessible to study and cartography it seems hardly possible to define it unequivocally. This applies to "metasomatic formation". It is therefore necessary to clear up its semantic content.

"Formational" approach in the classification of metasomatism rests on the well established existence of groups of closely linked metasomatic rocks that methodically occur in various regions in an initial geological surrounding. Every such group is formed under the action of solutions of a determined genetic type. Admittedly there exist in nature a limited number of genetic types of hydrothermal solutions. The interaction of such a solution with rocks of diverse constitution determines formation of a group of metasomatic rocks we unite under the term "metasomatic formation".

Formulating the notion of "metasomatic formation" was first attempted by V.A. Zharikov [1956, 1968]. He believed that a metasomatic formation can be defined as a group of metasomatic facies elaborated in the course of one petrogenetic process (or a geological process genetically unique).

This definition was later made more precise by Jarikov et Omelianenko [1978]. They proposed to call metasomatic formation a natural group of metamorphic facies characterized by one determined mineral group and one determined geological position. Unfortunately this needs a complementary explanation : what should be meant by one only petrogenetic (geological) process or by a determined geological position ? Il fut proposé de désigner une formation métasomatique comme un ensemble

D.V. Rundqvist et I.G. Pavlova [1974] consider a formation of hydrothermal metasomatism as a variety of geological formation. It can be defined as a group, obeying a statistically stable norm, of metasomatic rocks linked by a general structure. Hence the structure of a formation is perceived as a type of spatiotemporal linkage reflecting the rocks' arrangement.

B.I. Omelianenko [1978] defined a metasomatic formation as a group of metasomatic rocks characterized by a series of statistically stable features continuously occurring within a metalliferous province and are repeated in other regions in similar geological conditions. Among these features : the place occupied in the region's geological evolution; the nature of relations with a determined type of magmatism, the details of mineral and chemical composition; metallogenic and geochemical specialization; conditions of localisation; bormality of the metasomatites' structure.

These features not only characterize metasomatic rocks as such, but also petrogenetic processes. Some may coincide in different types of formation, but they in their entirety are a necessary and sufficient condition to decide belonging to a "formation" of metasomatites [Omelianenko, 1975].

O.N. Griaznov [1992] proposes to call "metasomatic formations" a constant association of metasomatic rocks resulting from a unique petrogenetic process in time and space.

Typically all the authors just cited give the same meaning to the concept of metasomatic formation, although realizing that no definition can be given of it excluding any different interpretation.

Metasomatic facies proves to be a singular element of classification. According to V.A. Zharikov [1956, 1959, 1968], it is a group of metasomatic rocks formed in different zones of a unique metasomatic column, in fact, a complex of modification linked to the action of a determined type of solution on rocks initially identically composed in determined external conditions (temperature, depth, degree of mobility, activity of perfectly mobile components). According to B.I. Omelianenko [1978] the metasomatic facies is a group of metasomatic rocks forming a determined metasomatic column. Obviously the former definition is based on causal characteristics, whereas the latter is based on derived, but directly observed characteristics. However, the two definitions are equivalent. If each facies is described by a cluster of metamorphic zones, a metasomatic formation is described by the entirety of facies composing it.

Hydrothermal cycle, its stages, its link with magmatism and mineralization.

There exist between the different types of formation of metasomatites diverse mutual spatiotemporal and genetic relations. Some of them are successive derivatives of one postmagmatic activity, others belong to stages of different ages. It is by evidencing the relations between metasomatites of different types of formation and magmatism that determines this successful use of the results of cartography for metallogenic analysis, previsions and search for deposits. It is very important for the solution of these questions that one comprehends the most general laws of hydrothermal metasomatic processes.

Analysis of metasomatic development in the tectono-magmatic evolution of the pleated regions has shown that to each stage of a tectono-magmatic cycle, as understood Y.A. Bilibine [1955] et I.G. Magakian [1959] corresponds a finished hydrothermal cycle [Zharikov and Omelianenko, 1965]. Hydrothermal cycle means a finished period of hydrothermal activity characterized by evolution according to certain laws of the constitution and properties of magmatic solutions. Many confirmations have been published [Skoroskelpine, 1974; Velichkine and Volovikova, 1978]. The notion of hydrothermal cycle permits not only to describe a natural group of hydrothermal metasomatic processes but also to establish a parallel between a hydrothermal activity and other geological processes, notably magmatism. Such a confrontation implies that a hydrothermal activity may be linked to concrete magmatic massifs as well as a whole cluster of magmatic manifestations of each definite stage of a tectono-magmatic cycle.

Most of the known types of metasomatites are characterized by their links with such and such magmatic formations. In some cases the link is direct, genetic, expressed in the coincidence of the metasomatites with magmatic bodies of a determined composition or with their exocontacts. In other cases the metasomatites can be very far from the magmatic bodies at the time of their formation. A link is also observed between metasomatite type and the nature of the formations nearest to them in age. In such cases we speak of paragenetic links. There is no doubt about the noted interdependencies when are most generally considered the details of the hydrothermal metasomatic formations developed in regions with a magmatism of granitoid, alcalin, ultrabasic alcalin, intrusive gabbroid or, for instance, in regions with an acid or basic vulcanism.

Terms used to designate metasomatic formations. The most appropriate are those which as soon as they appeared, designated a cluster of rocks formed under the influence of solutions of a determined type (for instance magnesium skarns, gumbeyites, lisites, fenites). Some have acquired a formational meaning, although they initially designated a rock of determined constitution and outward aspect. Such are for instance the names greisen, skarn, beresite. Their use in broad

formational sense is rightly objected by some researchers [Rundqvist *et al.*, 1971], who would prefer a term to keep its initial meaning and want to separate the notions of greisen and formation with greisen, beresite and formation with beresite, etc. This seems justified, for it avoids different interpretations of one and the same concept. Only, if at the beginning of an article it has been stated that the term is used in the formational sense and if the subject is constantly formation, there is no need to repeat the word again and again.

Unfortunate seems the use of terms alluding to the most typical newly formed mineral (albitised granites, metasomatites with chlorite-tourmaline) or to an added chemical element (silico-alkaline or potassic metasomatites). Some of these have traditionally been used in a formational sense, others have acquired this sense in the last few years. A great part has invaded geological literature to such an extent that replacing them would bring confusion and rejection by most researchers. In the proposed classification we have resorted to terms based on a different principle. Admittedly this classification shows inevitable insufficiencies. But its unity is preserved, since all the terms are given a formational meaning.

Geological literature sometimes uses different terms for the same metasomatites. We have used the most wide-spread and put the others in parentheses.

Metallogenic specialization of metasomatites. There may exist between the processes of metasomatic transformation and the mineralized deposits the following relations :

- a) they may appear simultaneously, mineralization being located in determined zones of the metasomatic column;
- b) mineralization occurs a little later than the metasomatites as a result of a common hydrothermal process (type of associated mineralization);
- c) metasomatites and mineralization are not genetically linked, although the former serve as a surrounding favorable to mineralization.

The classification thus distinguishes synchronous, associated and superposed metalliferous elements. The synchronous type is characteristic of deposits with rare metals, formed at high temperature; the superposed type is typical of the skarns, which constitute a chemically active surrounding largely favoring precipitation of metalliferous elements with superposition of acid leaching processes; the associated type characterizes the overwhelming mass of deposits.

Associated metamorphic processes. Formation of metasomatites of one or the other formational type results from processes of very long duration. This is shown, in particular, by the important aureoles of metasomatic transformation

and, frequently, the complete achievement of observed metasomatic reactions. It is easy to show that in order for metasomatic reactions to be achieved, a volume of solution is needed that is many times greater than that of the rocks submitted to transformation. In the course of this long time the solutions' parameters are constant enough and determine a rigorously determined sense of the metasomatic reactions, ending up in forming a zonally structured metasomatic body with a determined final composition. However, at the early stage of the hydrothermal process the metasomatic transformations usually change perceptibly. Although late associations usually develop less than the early ones, they can nevertheless complicate the structure of the metasomatites, particularly in the latter's central zones, replacing partly, or indeed completely in some places, the associations formed earlier on. Thus it is not rare for an argilisation to turn into hydromicatisation, shamositisation, carbonatisation and so on. Notably, a metalliferous mineralisation is a rule closely associated with the late mineral associations. Transformations linked to the final stages are usually called periveinous or mineral escorting.

One particular of associated metasomatic processes is the preference for the formation of one or, more rarely, two minerals, which is besides reflected in the names of these processes. A great inequality of distribution is even usual in the space of the newly formed minerals. They are clearly controlled in the fracturation and cataclasis zones superposed to the primary metasomatic zonality. A large part of the associated mineralisation is constituted by veins, microveins and cements of breaches. No metasomatic zonality is formed in a process of associated metasomatism. Most often associated mineral genesis happens through filling up the free space due to the pores by means of a determined mineral and replacement of minerals previously formed in the cushing zones. Contrary to rule, the limits of the zones of primary zonality cross the outlines of the development zones of the associated mineralisation. But the zonal distribution of associated mineralization clearly shows its much later formation compared to the metasomatites linked with the main stage of the process.

Knowledge of associated metasomatic processes typical of each formation may be very useful to that of metasomatic rocks and its applications. Unfortunately, information on this point is very scanty; hence the correspondent column in the classification requires important complements.

Table 13.1

Characteristic of metasomatic types of rocks

Type of metasomatic process	Type of metasomatite	Depth of formation	Link with magmatisme	Associated metasomatic process	Typical metalliferous elements			Typical parageneses of external zones
					Synchronous	Associated	Superimposed	
Lixivation acide	Solfatarian argillisites	Surficial	Acid volcanism	Carbonatization, montmorillonization, chloritization	Alunite, bentonite, zéolite, S	As, Hg, Sb, Cu, Pb, Zn, Ag, Au		Qtz+Kln, Qtz+H-Mic, Qtz+Mnt, Qtz+H-Mic+Mnt
	Hydrothermal argillisites	Surficial-hypobayssal	No concrete links with magmatic bodies	Séricitization, chloritization, hématitization, albitization		Pb, Zn, Cu, Mo, W, U, Hg, As, Au, Ag, Be, Sb		Qtz+Kln, Qtz+Ser, Qtz++H-Mic, Qtz+H-Mic+Mnt, Qtz+Mnt+Carb
	Hydromicacites	Surficial-hypobayssal	Areas of development of acid volcanites	Carbonatization, chloritization, hématitization, albitization		U, fluorite, Pb, Zn, Ag, Cu, Mo		Qtz+H-Mic, Qtz+Mnt, Qtz+Mnt+Carb
	Beresites	Hypobayssal	Areas of development of granitoids and volcanites	Pyritization, chloritization, carbonatization	Cu, Pb, Zn, Au, Ag	Au, U, Pb, Zn, Cu, Ag, Sb, Hg, As, Co, Ni		Qtz+Ser+Py, Carb+Ser+Py, Qtz+Carb+Ser+Py
	Quartz-sericite Chloritites	Subvolcanic	Areas of development of volcanites of intermediate composition	Chloritization, carbonatization, séricitization, chloritization, silicification		Cu, Zn, Pb, Au, Ag, Mo		Qtz+Ser+Chl+Py, Qtz+Ser+Py
	Gumbéites	Hypobayssal	Quartz syenite intrusive massifs	Séricitization, chloritization, carbonatization		W, Pb, Zn, Cu		Qtz+Orr+Ank+Phl+Py
	Secondary quartzites	Subvolcanic	Subvolcanic bodies of acid composition	Silicification, pyritization	Alunite, S	Cu, Al, S, Au, Ag, Mo, Hg, Sb, Pb, Zn		Qtz+Ser+Py, Qtz+And, Qtz+Om, Qtz+Alun, Qtz+Prl+Dsp
	Greisens	Hypobayssal	Leucogranite bodies	Tourmalinization, muscovitization, albitization, i-Potash feldspathization	Be, W, Zn, Cu	Sn, W, Mo, Be, Li, Bi, Cu, Cs, TR		Qtz+Ms, Qtz+Toz, Fl+Ms, Qtz+Ms+Fl, Phl+Fl+Sell
	Propylites	Surficial hypobayssal	Areas of development of granitoids and andesitic basalts	Adularization, epidotization, prehnitization, zéolitization	Zn, Pb, Cu	Ag, Au, Hg, Sb, As, Cu, Zn, Pb		Ab+Ep+Act, Ab+Ep+Chl, Ab+Chl+Carb, Ep+Chl+Carb, Ep+Qtz
	Quartz-feldspathites	Hypobayssal	Granitic intrusions	Potash feldspathization albitization, muscovitization	Sn, W, Mo, Cu, Zn	Sn, W, Mo, Cu		Qtz+Kfs, Qtz+Ab, Qtz+Ab+Kfs
	Quartz-turmaline Chloritites	Hypobayssal	Feeble link with highly basic granitoids	Tourmalinization, séricitization, silicification		Sn, Cu, Au, As, Mo		Qtz+Tu+Chl+Ser, Qtz+Chl+Ser
	Quartz-kyanite muscovites	Abyssal	Areas of development of gneiss-migmatites complexes	Muscovitization	Al	Muscovite		Qtz+Sil, Qtz+Ky, Qts+Ms
	Ultrabasite serpentinites	Hypobayssal	Ultrabasites	Antigoritization		Chrysotile-asbeste		Spt+Mt, Spt+Chr
	Aceites (sodic low temperature	Hypobayssal	No concrete links with magmatic bodies	Carbonatization, chloritization, hydromicacization, silicification	P	U, Th, Zr, Mo, Au, Pb, Zn, Ba		Ab+Ank+Hem, Ab+Chl+Hem, Carb+Ap, Ab+Qtz+Hem, Ab+Ap+Chl(Ank)+Hem

Carbonate-chlorite orthoclases	Hypabyssal	Weak link with subalkaline granitoids	Carbonatization, chloritization, pyritization, silicification				Or+Carb+Py, Or+Chl+Hem, Qtz+Or+Carb+Py
Albitites (apogranitic)	Hypabyssal	Granitic fissural intrusions	Micratization, fluoritization, silicification	Li, Ta, Nb, TR, Zr, Be, Sn, W			Ab+Fl, Ab+Qtz+Fl, Ab+Qtz+Ms, Ab+Qtz+Mc
orthoclases (apogranitic)	Hypabyssal- subvolcanic	Granites granite-porphyrines	Muscovitization				Kfs+Qtz+Bt
Albitites of contact zone of nephelinitic syenites	Hypabyssal	Nephelinitic syenites	Fluoritization, calcitization	Nb, Ta, TR, Th, Zr			Ab+Acm, Ab+Acm+Rbk, Ab+Bt, Ab+Astr, Ab+Ne+Acm
Nephelinitic	Hypabyssal	Alkalino-ultrabasic massifs	Phlogopitization, magnétitiza- tion, apatitization, libénériza- tion	Al			Ne+Px, Ne
Fénites	Hypabyssal	Nephelinitic syenites	Albitization, zéolittization, carbonatization			Phlogopite	Ne+Px, Ne+Kfs+Px, Kfs+Ab+Px, Kfs+Ab+Hbl, Ab+Kfs+Bt, Kfs+Ne+Bt
Two feldspars	Abyssal	No concrete links with magmatic bodies	Silicification, muscovitization, chloritization	Ta, Nb, Zr			Mc+Ab+Qtz+Acm, Mc+Ab+Qtz+Rbk
Microcline-biotite	Abyssal	Feeble link with ultramafic potassic granites	Albitization, muscovitization, silicification	Be, U			Mc+Bt, Mc+Ab+Bt
Albite-aegyrine (sodic)	Abyssal	No concrete links with magmatic bodies	Carbonatization, biotitization, hematitization, silicification, chloritization		U		Ab+Acm, Ab+Acm+Rbk, Mt+Rbk, Mt+Acm, Qtz+Acm, Ab+Ep+Chl, Qtz+Ab+Acm+ +Rbk, Ab+Mc+Acm
Mica carbonatic	Hypabyssal	Marked link with nephelinitic syenite intrusions	Carbonatization, zéolittization	Nb, Ta, TR, Zr			Lib+Carb, Lib+Zeol+Carb, Lib+Mc+Carb
Carbonatic chloritites	Subvolcanic	Feeble link with dacitic and liparitic porphyries	Polish feldspathization silicification, sulfuration, carbonatization	Pb, Zn, Cu			Chl+Carb, Chl+Carb+Ser, Chl+Qtz, Chl
Amphibole chloritites (ouralites)	Hypabyssal	Marked link with basic and ultrabasic intrusions	Chloritization, carbonatization, serpentinization	Fe, Ti, V, Pt, Pd, P, Cu, Ni			Act+Spr, Act+Chl, Act+Zo, Spr+Zo
Ouralites	Hypabyssal	Link with basic and ultrabasic intrusions	Biotitization	Cr, Fe, Ti, V, Pt, Pd		P, Cu, Ni	Hbl+Ti-Mt, Hbl+Bi
Phlogopitites	Hypabyssal	Link with ultrabasic alkaline rocks	carbonatization	Phlogopite			Phl, Phl+Px
Kamafortites (nelsonites),		Marked links with	Calcitization	Fe, P		Nb, Ta, Zr	Cc+Mt+Ap+(Fo, Di, Acm,

magnéstienne

Métasomatose calco-r									
foskorites apatitit rocks	Hypoabyssal	ultrabasic alkaline rocks							Phl, Rbk, Akt)
Carbonatites	Hypoabyssal	Marked links with ultrabasic alkaline rocks	Amphibolization, phlogopitiza- tion, chloritization, sulfuration	Nb, Ta, TR, Zr, Th	Phlogopite				Carb+Fo, Carb+Acn, Carb+ +Di, Carb+Mel+(Phl, Ap)
Magnesian skarns of magmatic stage	Abyssal hypoabyssal	Link with granitization and intrusions of various composition	Phlogopitization serpentinization calcitization	Fe Lazulite	Fe, Cu, Zn, B Phlogopite	B, Pb, Zn, Cu, W, Mo, Sn, Be			Fo+Spl+Carb, Px+Spl+Cc, Px+Pl, Px+Or, Fo+Px+Spl, Px+Pl+Scp, Px+Phl, Px+Prp
Magnesian skarns of postmagmatic stage	Abyssal	Link with early processes of post granitization	phlogopitization serpentinization, calcitization humitization, amphibolization						
Autoreactional skarns	Hypoabyssal	Link with peridotites, alkaline ultrabasic rocks	Actinolization, phlogopitization epidotization		Fe, Cu Phlogopite				Mtc+Mel, Px, Px+Grt, Act+Ep
Olivinic and pyroxenic	Hypoabyssal	Link with gabbros- peridotites massifs	Amphibolization, phlogopitiza- serpentinization	Fe, Cr?, Pt?					Fo, Px, Fo+Px
Calcic skarns	Hypoabyssal et abyssal	Link with granites, gabbros and syénites	Andraditization actinolization, epidotization magnetitization						
					Fe, Cu, As, Co	Sn, W, Mo, Pb, Zn, Cu, Au, Ag, B, U			Px+Grt+Wo, Px+Grt, Grt+Ep, Px+Ep

CHAPTER 14

Physico-chemical systematization of metasomatic formations

An assemblage of metasomatic rocks formed in a determined type of geological processes (i.e. to metasomatic formations) is characterized by a completely determined complex facies (association of metasomatic minerals), which corresponds to characterized intervals of importance of the main parameters of mineral formation. Attempts were therefore natural to classify metasomatites according to the variation of these parameters, amongst which temperature and regime of acido-alkalinity of the solutions exert the most substantial influence. As example may serve the classification of N.U.Bardin and V.S.Popov [1991] in which the types of metasomatic rocks are classified according to temperature and pH of the solutions. The authors disclaim the efficiency of using the formation approach and operate with the terms “types of rocks and facies”. This approach coincides with the position of American geologists who generally do not employ the term “formation” for assemblages of metasomatic rocks. In our opinion the notion of “metasomatic formation” is informative to the extent that it gives a clear presentation of the whole complex of geological and physico-chemical conditions of the formation process, of the links of metasomatism with the other geological processes (magmatic, tectonic, ore formative). For instance, it is quite understandable that greisens are formed from highly fluoric fluids in connection with granite intrusive magmatism in regions of orogenesis and tectono-magmatic activization. Although their facies vary in mineral composition and initial replaced rocks, they naturally unite in a distinctly marked single genetic group of rocks.

Unlike the formation, metasomatic rocks, as has been shown in the preceding chapter, are distinguished in mineral composition: quartz-sericitic, quartz-feldspathic, carbonate-chloritic, tourmaline-chloritic, quartz-alunitic, etc. In most cases these designations correspond to metasomatic facies, i.e., families of rocks formed in similar physico-chemical conditions and characterized consequently, by similar parageneses of minerals. The facies of the metasomatites are extraordinarily varied, since depending on many factors (temperature, acidity-alkalinity, fugacity of oxygen & carbon dioxide, composition of replaced rocks). In natural conditions, however, are found a

limited number of facies combinations formed jointly and steadily repeated in a definite geological surrounding (i.e. metasomatic formations). Despite a marked geological orientation to isolation of the formations, the latter are characterized by the limits of the variations, proper to each of them, of the physico-chemical parameters, above all, temperature and acidity of the solutions. These limits get blurred, often the fields of neighbouring formations are partly cut off, but all, in well-known approximation, may be approached by regions in the space of physico-chemical parameters.

Enumeration of one universal genetic classification of such an extensive & varied group of geological objects such as the metasomatic formations, is doomed to failure. Systematization is possible on a limited number of parameters with a definite purpose. We attempted systematization of formation in the spirit of D.S.Korzhinsky's idea of the acid-alkaline evolution of hydro-thermal solutions. As basis, take the principle of the diagrams from the work of A.V.Zotov et al. [1983], N.U.Bardine and V.S.Popov [1991]. In view of the fact that metasomatic processes occur in very wide limits, variations of temperature from less than 100°C to the temperature of melting of rocks (700-1200°C) in comparing the formations as to acidity of formation of their mineral associations with utilization of pH indicator there arise difficulties in the calciculation & comparison of the pH value for the different temperatures. Therefore, we have employed to construct the diagram (fig.14.1), as indicator of acidity-alkalinity, the relation of gross activity of one-valenced or two-valenced bases in the solution to the activity of the proton. In such an approach there is no need of a quantitative scale of acidity and one may be content with a qualitative diagram. In order approximately to characterize quantitatively the formation field, on the abscissa axis are indicated benchmark pH values after data of G.P.Zaraisky [1989].

Most boundaries of these fields present themselves as monovariant of equilibrium of mineral phases in the presence of the solution. Part of them is displayed on the experimental data existing in the literature; another part, on the basis of interpretation of geological data and paragenetic relations of minerals. It is well known that concentration of chemical components in the solution is based on their equilibrium with corresponding minerals of the rock. The obtained arrangement of the field on the diagram corresponds on the whole to the interrelations of natural metasomatic formations. On the diagram are shown four main groups of metasomatites, reflected basically in the variations of acidity-alkalinity of the solutions: 1) the most acid (secondary quartzites), in which from aluminosilicates there is stable kaolinite, in which Al is contained only in coordination 6; 2) less acid (beresites, greisens) with muscovites, containing Al in two coordinations (4 and 6); 3) perineutral metasomatites, in which there are stable framework silicates (feldspars and zeolites) with Al only in coordination 4; 4) alkaline metasomatites with feldspathoids (Al coordination

= 4 and Al/Si ratio higher than in feldspars and zeolites). Rather clearly are distinguished on the diagram the fields of high temperature metasomatites, bordering on those of middle temperature on the level of about 400°C. The boundary between middle and low temperature metasomatites is established a little above 200°C. To those of high temperature are related argillizites, quartz-kaolinitic facies of secondary quartzites, hydromicaceous facies of beresites, calcite-albitic facies of propylites and partially gumbeyites.

Evolution trends of parameters of fluids and the corresponding succession of metasomatic formations in the course of development of magmatogene hydrothermal systems, indicated on the diagram mark an increase of acidity of the fluids in the course of time (arrows are directed from early to late formations). In high temperature systems the trends are almost vertically oriented, reflecting a great temperature gradient, but in low temperature systems the position of the trend is nearly horizontal owing to the small gradient of temperature. It is essential that a maximum of acidity of the fluids and solutions should occur in various systems at various temperatures: 150-250°C in propylite-beresitovic and propylite-argillizitic ranges, 300-400°C in the range of K-feldspar metasomatite- secondary quartzites, 400-500°C for the successive hornfels-skarn-greisens, 700-800°C in metasomatites of alkalino-ultrabasic magmatic complexes. At the end of the pointer-marked trends occurs an inversion of alkalinity of fluids (late low temperature alkaline stage according to D.S.Korzhinsky), which has not been indicated lest the diagram would be overloaded. The differences of the temperature inversion show that apart from temperature, acidity of the solutions is limited to a certain undulatory function, linking the solution's acidity with the dynamics of its filtration through the rocks and with the solution-rock interactions.

The proposed outline presents itself as an attempt at systematizing the main metasomatic formations. It permits a detailed elaboration by means of isolation of facies or new formations in the limits of marked fields. For instance, in the field X of united formation of albitite zones of deep breaks and albitites, there are peri-ore metasomatites in gold-ore deposits. Some specific groups of metasomatites extend in the fields of the described formations. For example, quartz-turmalinitic in greisens, carbonate-orthoclastic, in gumbeyitic and so on.

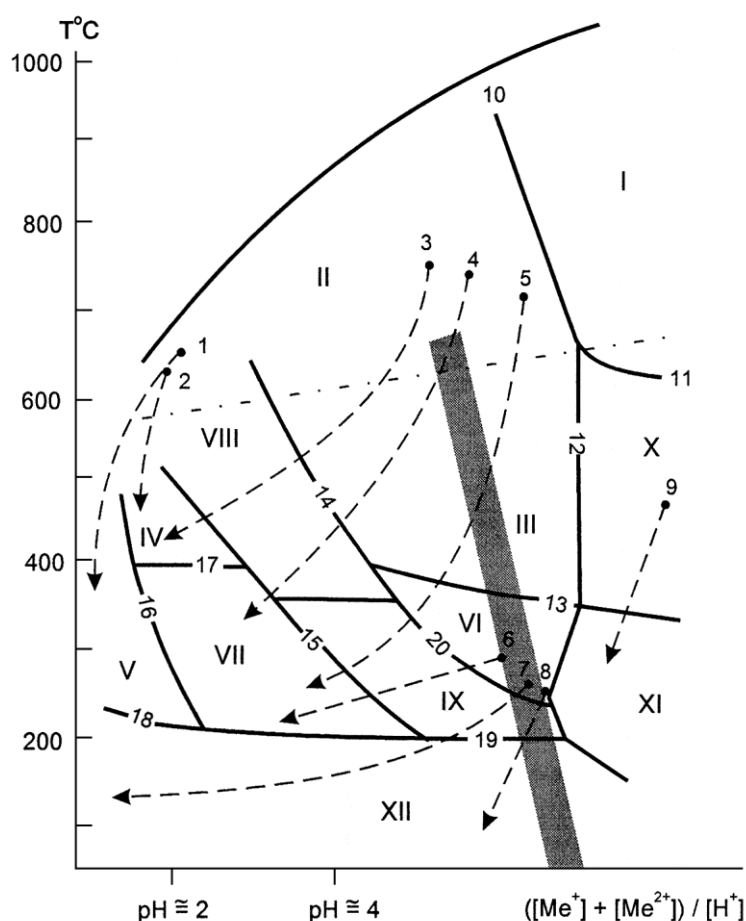


Fig. 14.1. **Phase diagram (T-pH) of important metasomatic families.**

Continuous curves – field limits of families (I – XII) and limit rock-magma; stroke line – limit between magmatic (above) and postmagmatic (below) metasomatic stages; - broken lines – trends of metasomatic processes (1 – 9); shaded strike – approached location of neutral and near-neutral solutions.

Family fields: I – fenites; II – magnesian skarns; III – calcic skarns; IV – greisens; V – secondary quartzites; VI – propylites; VII – berezites; VIII – quartz-Kfeldspar metasomatites; IX – gumbeites; X – alkaline metassomatites (aegyrine-albite, albitites, microclinites); XI – aceites; XII – argillisites.

Evolution trends (1 – 9): 1 – “porphyry” (quartz-feldspars metasomatites – secondary quartzites); 2 – greisens; 3 – skarn-greisen; 4 – skarn-berezite; 5 – skarn-propylite-berezite; 6 – propylite-gumbeite-berezite; 7 – propylite-argillisite (in epithermal deposits); 8 – propylite-argillisite (in geothermal fields); 9 – alkali-feldspar.

Limits of univariant fields (10 – 20): 10 – $\text{Fsp} + (\text{K,Na})_2\text{O} = \text{Fspd}$; 11 – $\text{Aeg} + \text{H}_2\text{O} = \text{Rbc}$; 12 – $\text{Cpx} + (\text{K,Na})_2\text{O} = \text{Aeg}$; 13 – $\text{Di} + \text{H}_2\text{O} + \text{CO}_2 = \text{Act} + \text{Chl}$; 14 – $\text{Ab} + \text{CaO} = \text{Pl}$; 15 – $\text{Ms} + \text{K}_2\text{O} = \text{Fsp}$; 16 – $\text{Kln} + \text{K}_2\text{O} = \text{Ms}$; 17 – $\text{Ms} + \text{H}_2\text{O} = \text{Ser}$; 18 – $\text{Dsp} + \text{Qtz} + \text{H}_2\text{O} = \text{Kln}$; 19 – $\text{Ab} + \text{H}_2\text{O} = \text{An}$; 20 – $\text{Ank} + \text{Qtz} + \text{MgO} = \text{Cc} + \text{Chl} + \text{CO}_2$.

CHAPTER 15

Metasomatites of alkaline ultrabasic and alkaline magmatic complexes

15.1. Fenites

Definition. Fenites are high-temperature metasomatites associated with magmatic rocks of annular complexes of an alkaline ultrabasic carbonatite formation. They were first described in the Fen massif (Norway) [Brogger, 1921]. Annular alkaline ultrabasic complexes with carbonatites are confined to cratons and their marginal parts.

In the last decades was determined yet another formation type of carbonatites confined, differently from annular complexes, to deep, extended, fracture zones of folded belts [Ginsburg & Samoilov, 1983]. Alkaline rocks linked with carbonatites of that type are formed in deep parts of the earth crust, and with them are also associated fenites and silico carbonate metasomatites [Sobachenko & Gundobine, 1993].

To the fenites, E.Heinrich [1985] and recently N.I.Bardina & V.S.Popov [1994] relate also metasomatites at the magmatic stage, formed with intrusion of nepheline and alkaline syenites, on ultrabasic, alkaline-ultrabasic and alkaline magmatic rocks of the preceding phases of intrusion, and also on alkaline enclosing rocks. In this case all these metasomatites are considered as facies of fenites on different replacing rocks: silicic, ultrabasic and alkaline, as well as carbonate rocks.

If we hold on to the initial acception of this notion, the fenites are then high-temperature alkaline metasomatites formed at the magmatic stage at the time of intrusion of alkaline rocks into silicic rocks, granites and granitogneisses, enclosing alkaline ultrabasic annular massifs with carbonatites.

Nowadays have also been investigated fenites around alkaline massifs (without carbonatites), around carbonatites (without alkaline rocks) and around kimberlites. Facies of fenites on sandstones have been described [Evdokimov, 1982] but alkaline-silicate metasomatites, accompanied by miaskitic syenites

and carbonatites of deep linear zones appear as facies of fenites on amphibolites and micaceous and clayed shales [Sobachenko & Gundobin, 1993].

Fenitization as well as processes of ijolitization, turyaitization and syenitization is a process of distinctly magmatic (progressive) stage, in which is formed on biotite amphibole and, further, pyroxene. In some places a zone of magmatic replacement is formed.

Distribution. Fenites, as well as other metasomatites of magmatic stage are more widely developed in hypabyssal massifs, in which dimensions of fenite aureoles equal those of the massifs themselves. In the Kola Peninsula in the massif of Ozernaia Varaka the thickness of fenites equals two thirds of the thickness of intrusive rocks, and in the Kovdor massif, 13% [Sergeiev, 1967]. In the Kovdor massif, the introduction of alkaline intrusions along an annular fracture at the contact of olivinites with enclosing gneisses was accompanied by a thick metasomatism of these and other rocks. As a result, along the outer contact was formed an aureole of fenites and fenitized gneisses with a thickness from 1.2 km (on the western slope of mount Votsu-Vaara) to 4.5-5km (on the southern slope of mount Pilkoma-Selga). In the Fen massif (Norway) fenites form western and southern aureole (fig.15.1), occupying 20% of the massif's thickness, in contact of melteigite ijolites, silico-carbonatites and carbonatites. Fenites of the cape Tur massif (Kola Peninsula) are formed in contacts of ijolite-melteigite and melilite rocks with granitoids and ijolite-melteigite with sandstones (fig. 15.2). Fenites of the Oka massif (Canada) form an almost continuous aureoles in the gneisses around the rocks of the melteigite-urtite series and around calcite carbonatites [Samson *et al.*, 1995]. Fenites, fenitized gabbro-pyroxenites and fenitized gneisses, granites and migmatites of the Poltava zone present themselves as a lengthened zone along carbonatites (fig. 15.3).

Metasomatic column. As rock-forming minerals of fenites appear potassic feldspar (orthoclase, microcline, sanidine) albite, nepheline, alkaline pyroxene (aegirine, aegirin-diopside, aegirine-albite, sometimes with addition of jadeitic mineral), alkaline amphibole (arfvedsonite, riebeckite, hastingsite, richterite); secondary mica (biotite, phlogopite), iron oxides; accessory: apatite, sphene.

The parageneses of these minerals regularly replace one another in the space from unaltered alumino-silicate rocks to magmatic alkaline ones, presenting themselves as successive zones of metasomatic columns of fenitization: 0. granites, granito-gneisses, gneisses, sandstones, micashists. 1. fenitized rocks. 2. pyroxene potash feldspar fenites. 3. nepheline-pyroxenic and anchimonomineral nephelinic fenites. 00 alkaline magmatic rock (melteigite, ijolite, nephelinic syenite) or carbonatite.

The facies of fenites on sandstones and granodiorites in the massifs of cape Tur have insignificant chemical developments [Evdokimov, 1982].

The predominant part of fenite aureoles, formed on granito-gneisses, represents fenitized rocks and feldspathic fenites; nepheline-pyroxenic and nephelinic fenites of rear zone abut to contacts with melteigites and ijolites. In contact of a rear (3) zone with alkaline magmatic rock, melting frequently takes place, resulting in an alkaline rock formed in situ, differing from the primary magmatic (of the same composition) by structure and geochemical peculiarities.

Chemism. The basic tendency to change in the chemism of the rocks forming successive zones of a column of fenitization of granito-gneiss is the removal of Si. At first, quartz disappears in the forward zones, in the feldspar fenites, SiO₂ concentrations diminish to 45%, and in the rear zones, desilication may lead to the fact that together with nepheline are formed non-silicated minerals, corundum, anatase, spinel, baddeleyite.

Fenitization, by definition, occurs as a result of a significant addition of alkali. Sodium concentrations monotonously increase from forward zones to rear ones, and potash concentrations may be maximal in the pyroxeno-feldspathic fenites. In relation to potash and sodium, fenites are divided, respectively, into sodico-potassic and potassic [Rubie & Gunter, 1983], of which the potassic, at comparatively low temperature, known exclusively in contacts with carbonatites, consist in orthoclase with magnetite or hematite, whereas the sodico-potassic, occurring in the contact with both carbonatites and alkaline rocks (melteigites, ijolites, nephelinic syenites) at higher temperature, consist in all the above-mentioned minerals of the fenites. The proportion of sodium and potassium in fenites depends upon the composition of magmatic rocks, source of fenitizing solutions. Fenites around epileucitic and calcicilitic syenites of the Murinskoie massif (Aldan) are characterized as Na₂O/K₂O = 0.15 to 0.40, while this ratio in fenites in contact with ijolites or nephelinic syenites is higher than the unity [Bardina & Popov, 1994]. In the classification they have proposed is taken into account the quantity of silica, as well as the total quantity of alkali, but, in particular, the mentioned potassic fenites are by them related to orthoclasites, i.e. to much later postmagmatic metasomatites.

In fenites of rear zones occurs a significant accumulation of alumina (up to 29%), which get fixed not only in nepheline but also in clinopyroxene (jadeitic mineral) [Tykhonenkova, 1967] and in arfvedsonite.

Physico-chemical conditions of fenitization. According to data of A.S.Sergeev [1967] melting of fenites in contact or proximity of big apophyses of intruding rocks testifies to the fact that temperature may reach 700 to 800°C. Experimental research places the temperature of stability of paragenesis of microcline-perthite + aegirine-augite, starting with 500°C [Zaraisky *et al.*, 1984], appearance of nepheline at 580 to 600° (the same authors), but disappearance in fenites of fluoric arfvedsonite, at 500±30°C [Kovalenko *et al.*, 1977].

On experimental and calculated data of N.Y. Bardine and V.S. Popov [1994] the pH of the fluid, in equilibrium with mineral associations of fenites, is not less than 8-10. With the method of measuring the pH of rocks in suspension of aureoles in exocontact it has been shown that a long interaction of alkaline solutions with gneisses leads to a decrease of pH of solutions to a value nearing 7 [Sergeev, 1967]. The gradient of chemical potentials of Ca and Na in a metasomatic solution is expressed in the direction of change of concentration of these components in the rocks of successive zones. The value of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in these rocks also grows in proportion to the proximity to the source of the solutions, ijolite or nephelinitic syenite, which is brought about by the high oxidation potentials of alkaline solutions.

Source of fenitizing solutions. The sources of fenitizing solutions must evidently be magmatic rocks with the necessary content of alkali; moreover, seemingly, these rocks were formed as a result of a sufficiently high degree of differentiation of initial magmas, because xenoliths of crustal rocks, entrapped in nephelinitic lavas, i.e. less differentiated derivative, do not experience fenitization [Le Bas, 1977].

As far as fenites are known around alkaline rocks, as well as in immediate contact with carbonatites (see fig.15.1, 15.3) the problem in discussion is whether ijolite or carbonatite is the source of solutions derived of fenitization [Morogan, 1994].

Change of composition of pyroxenes from successive zones of a metasomatic column of fenitization, from forward to rear zone, is characterized by two tendencies: (1) aegyrine $\rightarrow$ hedenbergite $\rightarrow$ diopside and (2) aegyrine $\rightarrow$ hedenbergite (fig. 15.4). In fenites of the cape Tur massif, the first of them (T_1 on fig. 15.4) is characteristic of apogranitic fenites, and the second (T_2) of aposandstones. However, both trends take place in fenites of the Fen massif (F_1 and F_2), although the fenitized rocks are exclusively granitogneisses. V. Morogan [1994] links the first one with ijolite-melteigite sources of fenitized solutions, but the other with carbonatites (?), as these trends go towards meeting trends ij and m.ij of change of composition of pyroxenes from successive differentiates of the melteigite-urtite series (diopside $\rightarrow$ hedenbergite $\rightarrow$ aegirine) in the first case and, in the second, trends dv of change of composition of pyroxene in rocks of the damkjernite-vibetoite series¹ (diopside $\rightarrow$ hedenbergite). In this way, two types of fenitization are distinguished: ijolitic and carbonatitic [Morogan 1994].

The main factors [Morogan, 1994] determining the ijolitic type of fenitization are: $\text{CO}_2 < \text{H}_2\text{O}$ (determining, in particular, scarcity in the fenites of

¹ Damkjernite is a nephelinite monchikite (alkaline lamprophyre, consisting in phenocysts of olivine, pyroxene- augite, titanium-augite, biotite and/or amphibole-barkevicite, kaersutite and basic mass, consisting of analcime, amphibole, pyroxene, biotite, sparsely nepheline, sodalite, cancrinite, leucite, hauyne); vibetoite is a calcic jacupirangite [Petrographic dictionary, Moscow: Nedra, 1981].

calcite and abundance of aqueous mafic minerals); high activity of alumina and comparatively low CaO activity; comparatively low FeO/MgO ratio, determining, in particular, the aegirine → hedenbergite → diopside trend of change of composition of pyroxene, and predominance of magnesian arfvedsonite; $\text{Na}_2\text{O} > \text{K}_2\text{O}$; relatively high fugacity of oxygen; and highly gradual fall of temperature (at great distance from the magmatic source).

The carbonatite type of fenitization is controlled on the contrary, by the following factors: $\text{CO}_2 > \text{H}_2\text{O}$, determining an abundance of calcite and scarcity of aqueous mafic phases, a very low activity of silicic-acid and alumina, a very high activity of CaO, a comparatively high FeO/MgO ratio (aegyrine → hedenbergitic pyroxene trend); however, phlogopite may form; the most various proportion of alkali and very progressive temperature gradient (at short distance from the magmatic source).

Discovery of soda carbonatites of Oldonio-Lengai and research of fluid inclusions in minerals of carbonatites [Samson *et al.*, 1995] testify that carbonatic magmas are enriched with alkaline, basically, sodium. A. Wolley [1982] links the process of fenitization with the evolution of carbonatitic melt, in the course of which process are liberated sufficient quantities of sodium. There are in fenitizing fluids a certain quantity of dissolved carbonates of alkaline metals fully really [Samson *et al.*, 1995], and CO_2 content in the fluid together with contents and ratio of alkali, temperature and pressure, appears as an important parameter, determining the composition of parageneses [Rubie & Gunter, 1983]. Despite the significant role of the content of carbon dioxide in the fluid, the significant addition of alumina in contact fenites contradicts the hypothesis linking fenitization to the action of alkalino-carbon dioxide aqueous solutions that form with leaching of $(\text{Na}, \text{K})_2\text{CO}_3$ from carbonatites [Le Bas, 1990]. Also the development of magnetite (hematite) – orthoclase rocks in contact only of carbonatites, without development of parageneses at higher temperature of fenites containing nepheline, permits to conclude that the source of fenitizing solutions is not carbonatites but alkaline or alkalino-ultrabasic rocks.

It has been possible in recent years to show [Rass 1986; Rass & *al.* 1996, 1998] that rocks containing melilite in alkalino-ultrabasic-carbonatite complexes present themselves as differentiates of initial mantle magmas of specific composition, with a Ca/Mg ratio higher than in the initial magma giving rise to the jacupirangite-melteigite-ijolite-urtite-nephelinic syenite serie. Most probably, melilite-containing rocks may also be the source of fenitizing solutions. Confirmation of this hypothesis is found in trends to change of composition of pyroxenes of melilite effusive rocks and fenites of cape Tur: in the successive differentiates of more calcicium-rich initial magma, the trend is from diopside to hedenbergite (see fig.15.4. T_m), on the whole, coinciding with the trend of the pyroxene of the damkjærnites-vibetoites of the Fen massif; from

forward zones to rear zones of a metasomatic column of fenitization, the trend goes from aegyrine to hedenbergite (T_2) both trends encountering each other.

Experimental melts jointly with carbonatite and fenite of the Kovdor massif [Kapustine, 1990] led to occurrence of an alkaline melt, close in composition to a melilite-turyaite melt, which order of crystallization was wollastonite-melilite-nepheline, which also confirms the conjecture that the source of fenitizing solutions together with melteigites, ijolites and nephelinic syenites, may be the turyaites and okaites. This conjecture may clarify these peculiarities of composition and temperature of the formation of fenites, which contradict the notion of a carbonatite source of fenitizing solutions, in particular, the accumulation of alumina in rear zones of a metasomatic column of fenitization.

15.2 Metasomatites of alkalino-ultrabasic carbonatite massifs

Definition and geological position. The geological position of the metasomatites described in the present chapter is determined by the geological position of alkalino-ultrabasic-carbonatite complexes with which they are genetically linked. Annular alkalino-ultrabasic complexes with carbonatites, the silicate rocks of which are characterized by the $Na/K > 1$ ratio, are confined to cratons and their marginal parts; but complexes in which the ratio of alkali in the silicate rocks is reversed (i.e. $Na/K < 1$) are confined, together with old platforms, in phanerozoic ones and their marginal parts. In the last decades have also been recognized linear alkalino-ultrabasic-carbonatite complexes confined to deep zones of folded domains. As to annular complexes, their link is obvious with initial mantle magmas (isotopic relations; enrichment with rare elements, in particular Nb, Zr, Ti and Y, and also phosphorus); for linear complexes, this link is manifested only in Nb enrichment, but isotopic ratios testify to conditions existing at the base of the crust.

For magmatism of alkalino-ultrabasic carbonatite annular complexes is specially characteristic a sodic introduction of successive differentiates of at least 5 sub-series: ultrabasic rocks, pyroxene-nepheline alkaline rocks; melilite-bearing calcalkaline rocks, nephelinic and alkaline syenites; carbonatites (strictly speaking carbonatites and apatite-forsterite-magnetite rocks).

Considering their depth formation, alkaline-ultrabasic carbonatite complexes are divided into 1) effusive and subaerial, 2) hypabyssal, 3) mesoabyssal, 4) abyssal (already mentioned linear zones at the bottom of the crust).

Introduction of each magmatic phase is accompanied by metasomatism at magmatic stage of enclosing rocks and rocks of preceding magmatic phases.

The widest and brightest manifestation of metasomatites is in hypabyssal complexes, where their dimensions are comparable to those of the complexes themselves.

In the Kovdor massif (Kola Peninsula), which may be taken as standard for hypabyssal massif of a given formation, they occupy not less than half of the outcropping rocks [Ternovoy *et al.*, 1969] (fig. 15.5). The core of the Kovdor massif is composed of olivinites, representing the first phase of intrusion. Relicts of olivinites (measuring from a few to tens of meters) are found amid pyroxene, mica-pyroxene, nepheline and melilite rocks, surrounding the olivine core. The quantity and dimension of these relicts at the massif's periphery gradually decreases. Alkaline rocks of the second intrusive phase form an almost continuous peripheral ring uneven in thickness. They represent homogeneous median-grained massifs of ijolites and ijolite-melteigites (in the southern part of the massif), heterogeneous middle and coarse grained ijolite-urtites partly recrystallized, and turyaites (in the northern parts of the massif). In the ijolites, ijolite-melteigites, ijolite-urtites are found xenolites of olivinites (and gneisses). Turyaites form in the northern part of the massif a semi-circular zone 0.6-1.0 km thick and 5 km long. In the east a big body of turyaites is linked with ijolites. In the turyaites are now and then found xenolites of olivinites with the same zonal phlogopite-pyroxenic fringes as around the xenolites of olivinites in the ijolites.

Introduction of alkaline intrusions in the annular fracture at the contact of olivinites with enclosing gneisses was accompanied with a powerful metasomatism of both rocks. Metasomatites formed on enclosing rocks of the complex (rocks of the frame, in particular: acid-granitogneisses), under the action of alkaline, calcic-alkaline or calcic solutions at the magmatic stage, are related to the formation of fenites and are described in section 15.1. It is thus convenient here to consider metasomatites: (1) formed on olivinites and peridotites during the intrusion of rocks of the jacupirangite-urtite series in the process of *ijolitization*; (2) formed on olivinites and peridotites during the intrusion of melilite-containing rocks in the process of *turyaitization*; (3) formed on magmatic and metasomatic rocks of pyroxenic and nepheline-pyroxenic composition during the intrusion of nephelines and alkaline syenites in the process of *syenitization*; (4) formed on magmatic and metasomatic rocks of olivine-pyroxenic, pyroxene-nephelinitic composition and melilite-containing rocks during the intrusion of carbonatites in the process of *carbonatization*.

All four mentioned processes are metasomatic processes of magmatic stage, i.e. occur at increased temperature. With the formation of metasomatic columns of ijolitization and turyaitisation, parageneses of glimmerites (biotites) are replaced by pyroxene-nephelines or melilite-nephelines. With formation of metasomatic columns of syenitization a paragenesis containing phlogopite is similarly replaced by an anhydrous anchimonomineral pyroxenic zone. With the formation of a metasomatic column of carbonatization, parageneses with

tremolite and tetraferriphlogopites are replaced by parageneses with newly formed forsterites. The rear zone in the forming metasomatic column may be represented by melts of corresponding composition: ijolites (fig. 15.6), turyiaites, nephelinic syenites or carbonatites.

With introduction of alkaline intrusions on an annular fracture between olivinites and enclosing gneisses in the Kovdor massif, on internal contact has formed a continuous annular zone of apoolivinite metasomatites, (but in external contact, an aureole of fenites). The thickness of the zone of apoolivinite metasomatites reaches 3-4 km. With alteration of olivinites, parageneses of metasomatic rocks zonally replace one each other from the center of the massif to the periphery in the following succession: olivinite – phlogitized and pyroxenized olivinite – mica – nephelinized pyroxenite – pyroxene and nepheline-ijolite rock; and olivinite (often with monticellite) – olivine-melilite rock and/or melilitonite – melilite-phlogopite rock – melilite-nepheline rock – turyaite. Appointed successions present themselves as metasomatic columns of respective ijolitization and turyaitization of olivinites.

Successive zones of an infiltration metasomatic column of ijolitization of olivinites are above all represented in the south-south-eastern part of the massif, where their summary thickness approximates 2.5 km, but the ratio of thickness of successive zones from the least alterations to the rear ones is 49:29:15:8. Coincidence of the most prolonged section with the submeridional fracture [Krasnova & Sokolova, 1978] appearing as magma-internal channel (together with annular fractures), permits to relate this zoning to the vertical metasomatic zoning in the interpretation of V.L.Rusinov [1982]. On the pyroxene-phlogopite thermometer of L.Perchuk [1970] the temperatures of formation of rocks of the ijolitization column is 700 to 760°C for the forward and rear zones respectively (gradient: 60°C on 2.5 km).

Metasomatites of infiltration metasomatic zoning of turyaitization of olivinites in the district of northwestern profile prolonged on 0.9 km and with relative 50:30:20:13 thickness of successive zones coinciding with the annular fracture, the magma-internal channel. Vertical metasomatic zoning is a normal extended arrangement of various phases of metasomatites in vertical direction, occurring as a result of filtration through rocks of a flow of solutions and perpendicular to the flow's direction. A possible model of formation is represented on fig. 15.5.

Change of mineral composition of metasomatites of the successive zones of a ijolitization column is characterized by the following stages: at the limit of phlogopitized olivinite and mica, olivine disappears; at the limit of glimmerite and nephelinized pyroxenite appears nepheline, which does not replace all phlogopite; at the limit of nephelinized pyroxenite and nepheline-pyroxene rocks phlogopite disappears.

For the mineral composition of the metasomatites of successive zones the columns of turyaitization are characterized by the following peculiarities: at the limit of phlogopitized olivinite and olivine-melilite rocks appears melilite; at the limit of olivine-melilite and melilite-phlogopite rocks disappears olivine and arises nepheline; at the limit of melilite-phlogopite and melilite-nephelinite rocks disappears phlogopite.

From the paragenetic analysis of these associations it appears that their regular replacement is due to the inert behaviour of Mg, Fe, Si, Al in dependence upon change of chemical potentials of Ca and Na, leading to modification of the minerals' composition. The composition of minerals of variable composition at the limits of metasomatic zones changes abruptly and almost imperceptibly inside each zone (fig. 15.7) [Rass, 1986]. These regularities testify to a primarily infiltration character of the ijolitization and turyaitization processes.

Modification of the chemism of rocks formed in successive zones of metasomatic columns of ijolitization and turyaitization of olivinites, is determined by removal of Mg and Fe (fig. 15.8). The gradient of chemical potentials of Ca and Na in metasomatized solutions is marked in directional modification of the content of these components in the rocks of the successive zones; moreover, the formation of all zones of the metasomatic column of turyaitization occurs with greater chemical potential of Ca than the formation of all zones of the column of ijolitization. The value of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in these rocks also grows in proportion to their proximity of the source of the solutions, either ijolitites or turyaitites [Rass, 1982]. Iron oxidation cannot be dependent upon the presence of a strong oxidizers (ions V_3O_5 , Cr_2O_3 , MnO , Co , etc.) whose quantity in the studied rocks vanishes a little [Kukharensko *et al.*, 1965] and, very probably, is determined by the presence of aqueous solutions of increasing alkalinity. Judging from the directional change of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio and the $(\text{Na} + \text{Ca})$ concentration in the successive zones of apoolivinite metasomatites, it is possible to consider an indisputable lowering of alkalinity (an increase of acidity) of the metasomatic solutions in proportion to their distance from the source. On the modification, in the coexisting minerals, of the TR/Ca , $\text{Y-TR}/\text{Ce-TR}$, $\text{Fe}/(\text{Fe} + \text{Mg})$ ratio (appearing as acidity indicators) it has been established [Rass, 1972] that on the background of common increase of acidity of the minerals' composition from the rear zones to the forward zones, a maximum gets fixed of the most acid compositions of minerals in the middle zones of the column.

With syenitization is linked apatitization, studied in detail in the Magan massif (north-western Siberian platform), 42 km² wide, formed in four intrusive phases: ultrabasites phase (olivinites, pyroxenites), melteigite-urtite phase (including also feldspar rocks, malignites and juvites), syenitic phase (nepheline and alkaline syenites) and carbonatites (rocks of the series of kamaphorites and

properly carbonatites). On 80% of the massif are situated rocks of the second phase, but apatite-pyroxene metasomatites coincide with annular peripheric zones from 60 to 70 m thick, in a length of about 219 km and an area of 5 km². Rocks are until 400m deep apatitized and metasomatized in different degrees. They lie between enclosing quartzites and ijolites. In the south-western and south-eastern parts of the massif, between apatite-pyroxene rocks and ijolites is a layer of pyroxenic phlogopitized rocks, probably representing phlogopitized pyroxenites and jacupirangites. Nepheline and alkaline syenites of the third phase of intrusion represent intermediate annular discontinuous layer in the northern part of the massif, parallel to which are noted apatitized ijolites. Linking of apatite-pyroxene rocks in the south with phlogopitized pyroxene rocks, in the north, with ijolites, and a detailed petrographic study of apatite-pyroxene rocks, their contacts with ijolites and with nepheline syenites have permitted [Kravchenko *et al.*, 1987] to consider in a certain measure the apatitized rocks of Magan as successive zones of a column of syenitization, arising at magmatic stage with intrusion of nepheline and alkaline syenites in early formed rocks of the jacupirangite-urtite series and apatitized pyroxenites,

In the study of mineral associations resulting from syenitization of preceding magmatic and metasomatic nepheline-pyroxene rocks are observed stable parageneses, regularly replacing one another in the following succession: $Px_i + Ne + Ap - Px_i + Kfsp + Phl + Ap - Wo + Kfsp + Phl + Ap - Px_s + Ap -$ nepheline syenite ($Px_s + Ne + Kfs$). Ijolite and/or nepheline pyroxenite are submitted to potassic feldspathization and phlogopitization with preservation of part of diopside (Px_i); with passage to the following zone there occurs a complete replacement of diopside and formation of wollastonite; the following (rear) zone, anchimonomineral “aegirinite” consisting of aegirine-diopside (Px_s) and in combination with apatites presents itself as ore zone. The described change of mineral parageneses occurs with increasing chemical potentials of Fe_2O_3 and Na_2O , i.e. with increased alkalinity and oxidation potential, with decrease of the CaO chemical potential. The change in the chemistry of rocks forming in successive zones of a metasomatic column of syenitization, as well as with formation of metasomatic columns of ijolitization and turyaitization, is determined by decrease of Mg and Fe.

In the study of mineral associations of the phlogopite complex of the Kovdor massif it has appeared [Rass, 1974] that they replace one another in the following succession: $(Ol) + Di + Phl + Ap$ (gigantogranularity) – $Tr + (Ap) + (Cc) - Ol + Tfphl + Ap + (Cc) - Ol + Ap + (Cc) -$ carbonatite ($Cc + Ap$) (fig. 15.9). Rocks of this metasomatic column develop into olivine, olivine-pyroxene and phlogopite-pyroxene rocks, magmatic and metasomatic rocks at the magmatic stages. Similar metasomatites are also well-known in the Odikhintcho massif (north-western Siberia), where with them are also linked ore-occurrences of phlogopite (zone of gigantogranularity of phlogopite-pyroxene rocks). On

consideration of mineral associations forming the zones of this column, one must note the presence, ordinary in them, of bimineral parageneses, which testifies to the inertia of only two components; and instability of the Ol + Px parageneses, which testifies to mobility of MgO. From diagrams of parageneses of a phlogopitic complex (cf. fig.15.9) it appears that to zones of empirical removal of the column correspond spots of the diagram $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$, successively replacing one another with an increase of chemical magnesium potential.

With the method of phase correspondence [Perchuk, 1970] is established the temperature of formation of gigantogranularity of diopside-phlogopite rocks, equal to 700-720°C.

Metasomatites at postmagmatic stage. Together with the above described metasomatites at magmatic stage, forming in processes of ijolitization, turyaitization, syenitization and carbonatization of earlier formed rocks, with intrusion, respectively, of melteigites and ijolites, turyaites, syenites and carbonatites, to the formation of metasomatites of alkaline-ultrabasic-carbonatitic complexes we must also relate such metasomatites at postmagmatic stage, each of these processes apparently forming at last at lowering of temperature. Moreover, if the nephelinization process proves local, and the postmagmatic metasomatic processes, accompanying turyaitization and syenitization, prove indistinct, the postmagmatic processes of carbonatization (taking place with temperature decrease of the solutions with corresponding replacement of higher temperature parageneses by lower temperature ones) have a sufficiently wide spreading and in a number of cases a great significance for ore-formation, especially for the genesis of phlogopitic deposits and ore occurrences.

Research with the method of paragenetic analysis of the replacement of mineral associations of postmagmatic metasomatites of alkaline-ultrabasic rocks of the Gulinskoie massif (north-western Siberian platform) in dependence upon change of chemical CaO potential and growth of H₂O potential has shown that heterogeneous processes characterizing these rocks, phlogopitization and cancrinitization [Epstein *et. al.*, 1961], formation of pyroxene-garnet and phlogopite-garnet rocks (autoreaction skarns) [Zharikov, 1968], and also hydromelilite rocks [Lapin, 1965] lead to the production of metasomatites, the rear zone of which is substantially carbonatic, and the distinction between which is determined by the composition of the replaced rocks. The repetition of paragenetic associations and the regularity of their change, the direction of change of ferruginosity of coexisting phlogopite and pyroxene permits to present them under the aspect of the following metasomatic columns, different facies of carbonatized rocks: 1) olivine-pyroxene rock (magmatic or metasomatic-magmatic stage), i.e. phlogopitized olivine-pyroxene rock, pyroxene-phlogopite,

porphyroblastic mica² phlogopite-calcite rocks. 2) Nepheline-pyroxene rock (at magmatic or metasomatic-magmatic stage), nepheline-pyroxene with melanite, phlogopitized and/or cancrinitized, phlogopite-melanite, phlogopite-calcite rock; 3) Melilite-containing rocks (at magmatic or metasomatic-magmatic stage), phlogopitized melilite-containing rock, hydromelilite-olivine, hydromelilite phlogopite, hydromelilite-calcite rock.

With chemical analysis of rocks [Epstein *et al.*, 1961] establishing different zones of above-adduced generalized columns is traced the displacement of figurative spots on the diagram (fig. 15.10), reflecting a tendency to convergence of composition of the metasomatites, facies on various initial rocks.

Link with mineralization. Alkaline-ultrabasic-carbonatic formation possesses on the whole a unique ore-potential; linked with it are important and very important deposit of apatite, phlogopite, vermiculite, rare and rare-earth elements. Metasomatic processes promote concentration and localization of these useful components.

We examined above the mechanism of formation of the apatite deposit of Magan, with syenitization of earlier formed pyroxene and pyroxene-nepheline magmatic and metasomatic-magmatic rock stages. The source of phosphorous is undoubtless in the mantle, which is shown in the spreading of accessory apatite in practically all differentiates of alkaline magmas and carbonatites. It has been experimentally established [Kogarko *et al.*, 1981] that phosphorous solubility in early alkaline differentiates is four times higher than in melteigites, and that in the differentiation arises a massive crystallization of accessory apatite, not forming, however, deposits or ore-manifestation. The latter only form with high range syenitization on a front of syenite intrusion. It was recently possible to count the fixed association of the gigantic Khibine massif of alkalino-ultrabasic carbonatic formations, and the genesis of gigantic apatitic deposits coinciding with them may be interpreted in the afore-mentioned manner.

All testimonies of alkaline-ultrabasic massif simply link the formation of industrial (with little iron and coarse grains) phlogopite in them with metasomatic processes. Indeed, any metasomatic process leads to the formation of metasomatites, in which are present phlogopitized rocks and, often, anchimonomineral glimmerites. In the massif of the Maimetcha-Kotuysk province (NW of the Siberian platform) have been distinguished [Prokhorova *et al.*, 1966] 5 types of phlogopite deposits, depending upon composition of phlogopite-containing rocks: 1) olivinite type; 2) apomelilite type; 3) diopside pegmatoid veins in apojacupyrangites, apoolivinites; 4) nepheline-pyroxene pegmatoid veins in apopyroxenites, apojacupirangites; 5) garnete-nepheline-pyroxene pegmatoid symmetric-zonal veins in nepheline-melilite rocks. As

² Porphyroblastic glimmerite is formed in the replacement of porphyrous rocks, particularly with melanephelinite.

regards solubility of these types in these or other metasomatites, it is expedient to consider jointly types 1 and 3, as well as 2 and 5.

To the 1-3 type it is possible to relate the phlogopitic Kovdor deposit [Ternovoy *et al.*, 1969, Krasnova, 1972] the Ebe-Iurakh section of the Odikhintsh deposit [Goldburg & Landa, 1963], the Kugda phlogopite occurrence [Egorov, 1964]. By comparing Mg, Fe, Ti content in phlogopites from successive zones of metasomatic columns of carbonatization it has been established [Rass, 1980] that the average ferruginosity of phlogopites decreases from forward to rear zones, although maximal ferruginosity is characteristic of phlogopite from intermediate zones. Average titanite of phlogopites decreases in the same direction. In such deposits may be distinguished two stages of metasomatism. In the first one, on intrusion of alkaline magma have formed pyroxene and pyroxene-phlogopite rocks, and occurred mobilization of Mg from olivinites and Al from ijolites, with potassium either mobilized from the phlogopite of magmatic rocks or, as fully mobile components are abundant, they occurred in the metasomatic solutions and with alkaline metasomatism have participated in the formation of phlogopite. In the second stage of phlogopite formation of deposit of the examined type occurred carbonatization of earlier formed metasomatites in recrystallization of phlogopite with decrease of ferruginosity and increase of the crystals' dimensions. Substantially phlogopite deposits are formed in the phlogopite-containing rocks at the postmagmatic stage. If one of the stages took place, ijolitization with mica formation, carbonatization of melanophelinites and ijolites, no concentration of industrial phlogopite would occur. Nepheline-pyroxene pegmatoid veins (4 types), phlogopites in which is ferruginosity characteristic 31, seemingly appears a nepheline-pyroxene zone of a metasomatic column of ijolitization, with unlikely relation with industrial phlogopite. In the formation of phlogopite deposits linked with melilite-containing rocks (type 2 and 5) it is also possible to distinguish two stages: ijolitization of olivinomelilite rocks [Egorov, 1969] and, following them, carbonatization with formation of interfacial hydromelilite-containing zones. Thus, in conditions favorable to the formation of industrial coarse-grained underferruginosity (f from 6 to 14) of phlogopite in alkaline-ultrabasic massifs there occur 1) sufficient degrees of differentiation of alkaline-ultrabasic magmas; 2) sufficient development of metasomatic processes; 3) superposition of carbonatization processes on earlier formed metasomatites at the magmatic stage. Substantial (and industrial) concentration of niobium (pyrochlore), zirconium (baddeleyite) and rare earth (carbonates of rare earths), also linked with carbonatites of metasomatic genesis.

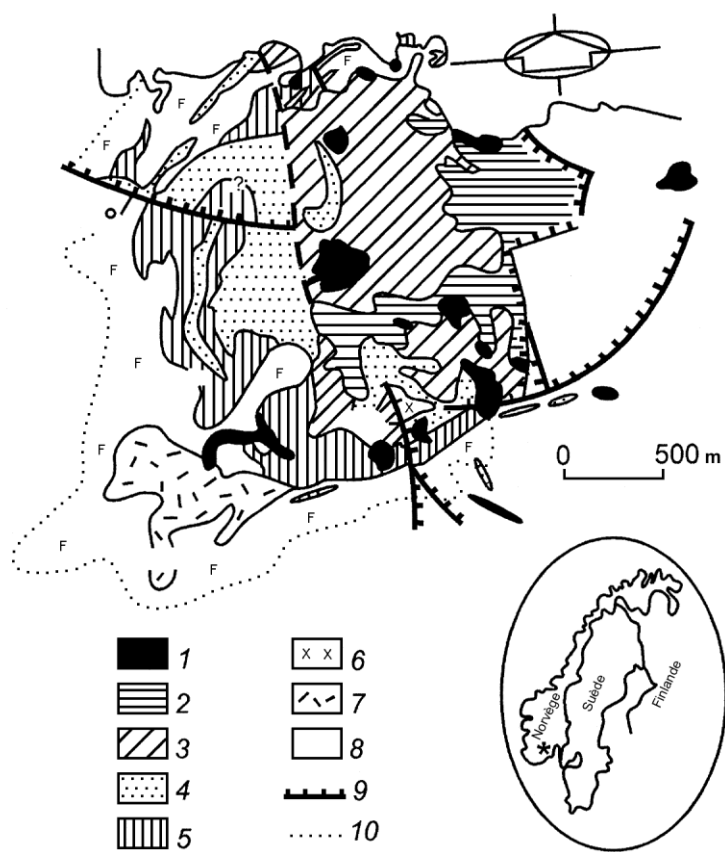


Fig. 15.1. Geological outline of the Fen massif [Mitchell, 1980].

1 – damkerite; 2 – ferrocarbonatites; 3 – dolomitic carbonatites; 4 – sövites (calcitic carbonatites); 5 – silicocarbonatites; 6 – vibetoites; 7 – urtites, ijolites, melteigites; 8 – archean gneisses; 9 – 10 – limits of fenites (F).

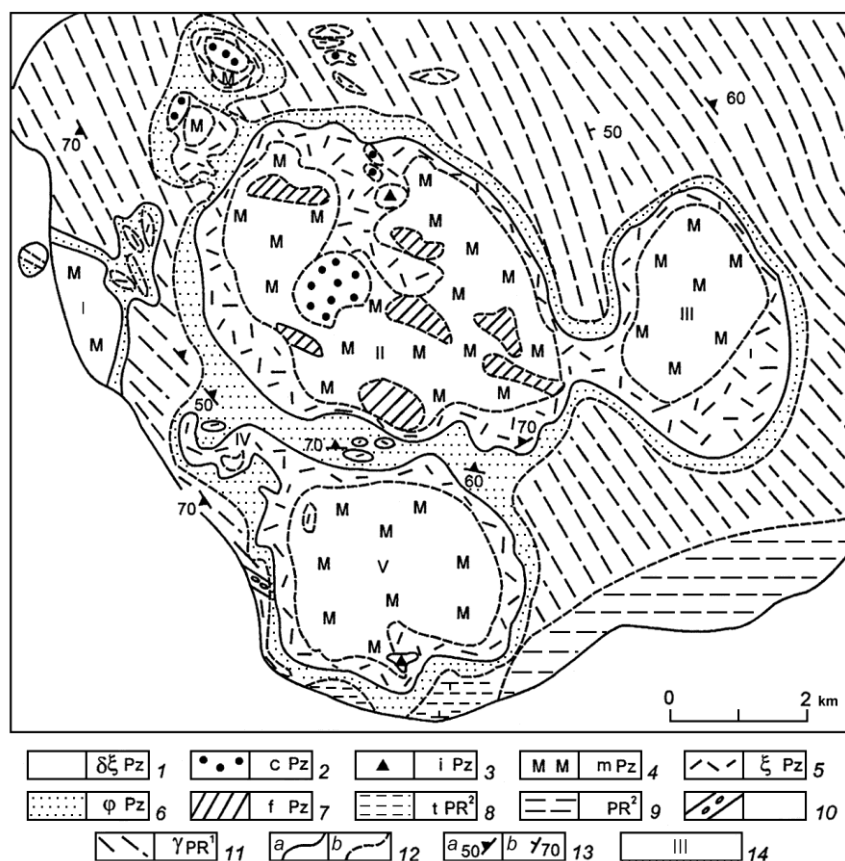


Fig. 15.2. Geological outline of cape Tur [Evdokimov, 1982].

1 – olivine melteigite porphyries; 2 – carbonatites and camaforites; 3 – ijolite-urtites of the second alkaline phase; 4 – undivided melilite rocks; 5 – ijolite-melteigites of the first alkaline phase; 6 – undivided fenites; 7 – pyroxenites; 8 – red sandstones series (terskoi??); 9 – aleurolites and quartzite-sandstones of the Tur formation; 10 – basal conglomerates; 11 – undivided granitoids of the Umbin complex; 12 – geological limits: a – observed, - proposed; 13 – bedding elements: a – banding of magmatites and metasomatites, b – layering and contacts; 14 – massifs (I – Kuznavolok, II – Central, III – Letnegorsk, IV – Gornozersk, V – Southern).

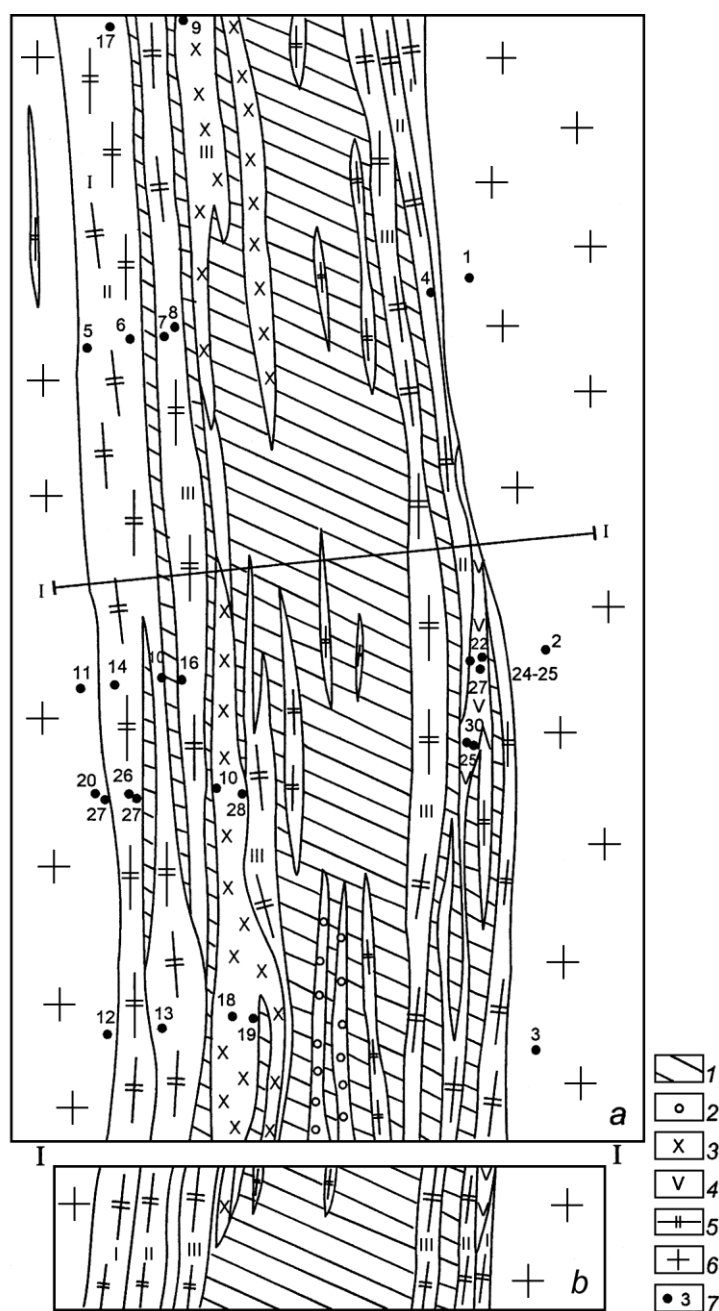


Fig. 15.3. Geological outline of the area of Novopoltavsk in Priazov [Kapustine, 1982].

a – central part of the carbonatite zone; b – cross section I-I; 1 – carbonatites; 2 – albitites; 3 – leuco-mesocratic nepheline-bearing fenites; 4 – fenitized gabbro-pyroxenites, often with nepheline; 5 – fenitized gneisses, granites and magmatites; 6 – archean granites and migmatites; 7 – sample locations.

I – III – fenites zones: external, medial and internal.

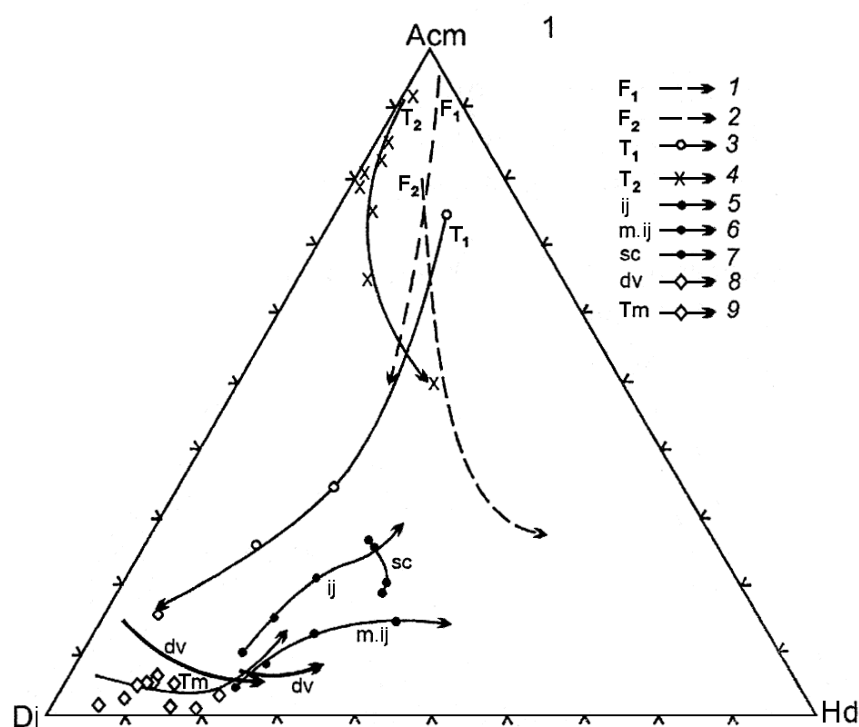


Fig. 15.4. Variations in pyroxene compositions.

F_1 , F_2 – successive zones of the column of fenitization of the Fen massif [Morogan, 1994]; T_1 , T_2 – successive zones of the column of fenitization of cape Tur massifs [Evdokimov, 1982]: T_1 – apogranite, T_2 – aposandstone; ij – ijolites, m.ij – melanite-bearing ijolites, dv – damkerites and vibetoites, sc – silico-carbonatites of the Fen massif [Mitchell, 1980]; Tm – melilite-bearing rocks of cape Tur massifs.

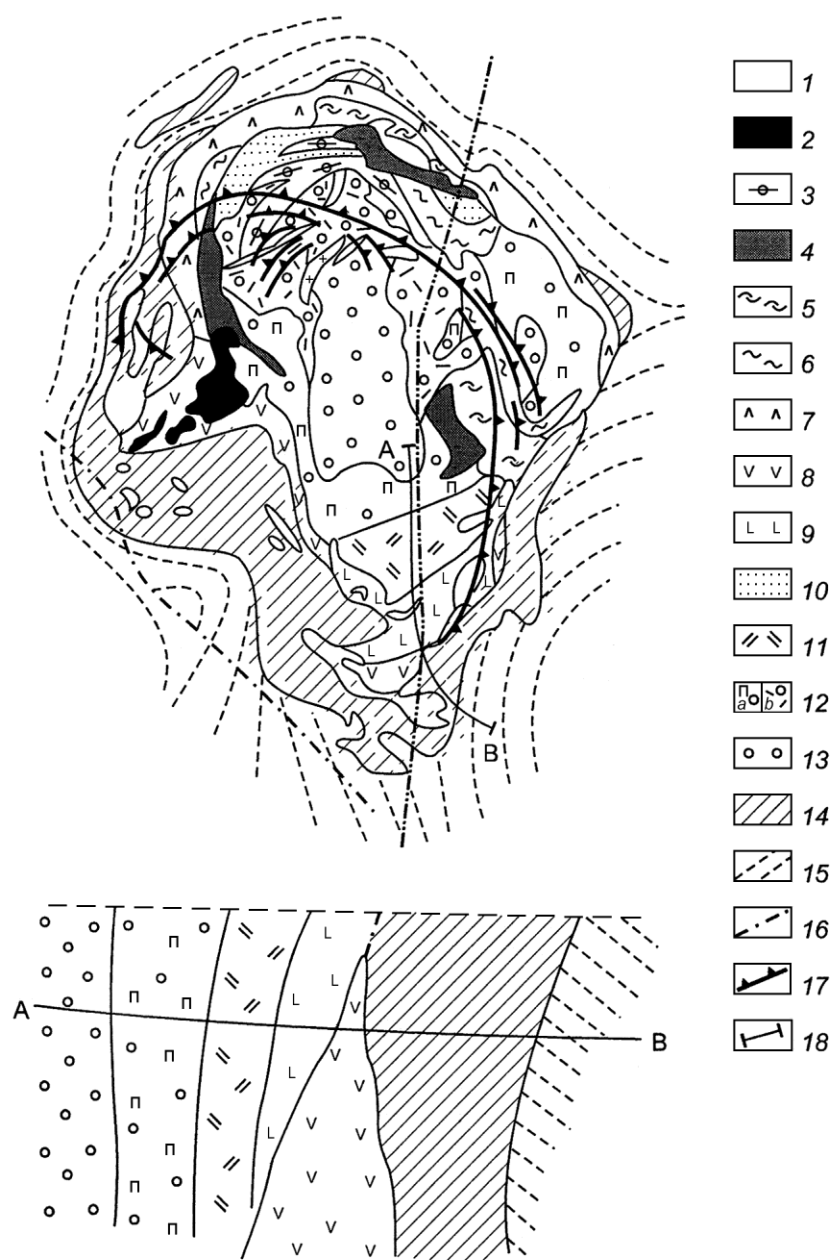


Fig. 15.5. Geological outline of the Kovdor massif [Ternovoi & al., 1969] with elements of a structural-tectonic map [Krasnova & Sokolova, 1978] and most plausible model of formation of vertical metasomatic zonation.

1 – carbonatites; 2 – apatite-forsterite-magnetite rocks; 3 – coarse-grained and coarse-grained-phlogopite-olivine rocks; 4 – garnet skarns; 5 – turiaites; 6 – melilitolites; 7 – ijolite-urtites; 8 – ijolite-melteigites; 9 – jacupirangites; 10 – monticellite-bearing rocks; 11 – glimmerites; 12 – pyroxenized and phlogopitized olivinites; 13 – olivinites; 14 – fenites; 15 – gneisses; 16 – phase I faults; 17 - annular faults; 18 – AB and CD - bore hole profiles accordingly; AB on figure below – present day erosional profile.

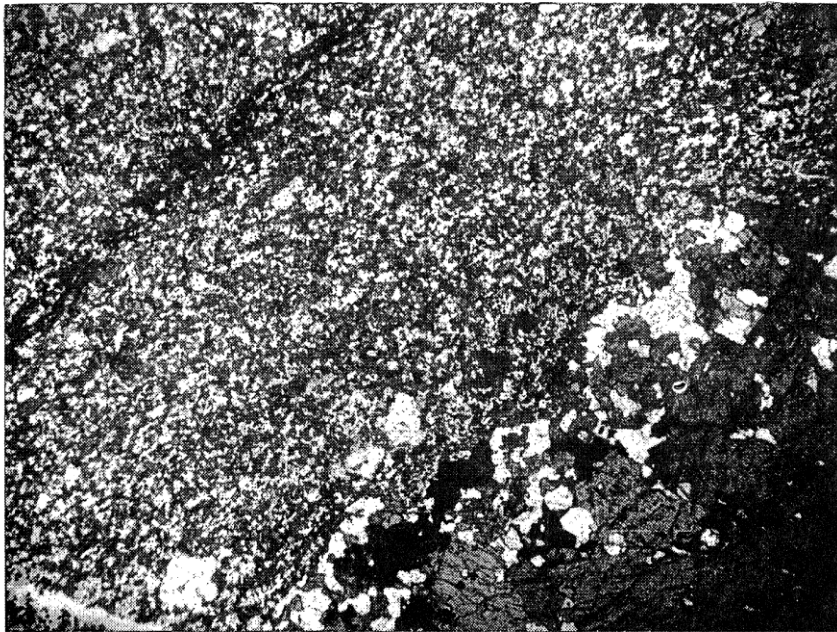


Fig. 15.6. Thin section trough ijolite veinlet of nepheline-pyroxene rock, Kovdor massif.
Thin section 1469a from the collection of A.A.Glagolev, magnification 30, natural light.

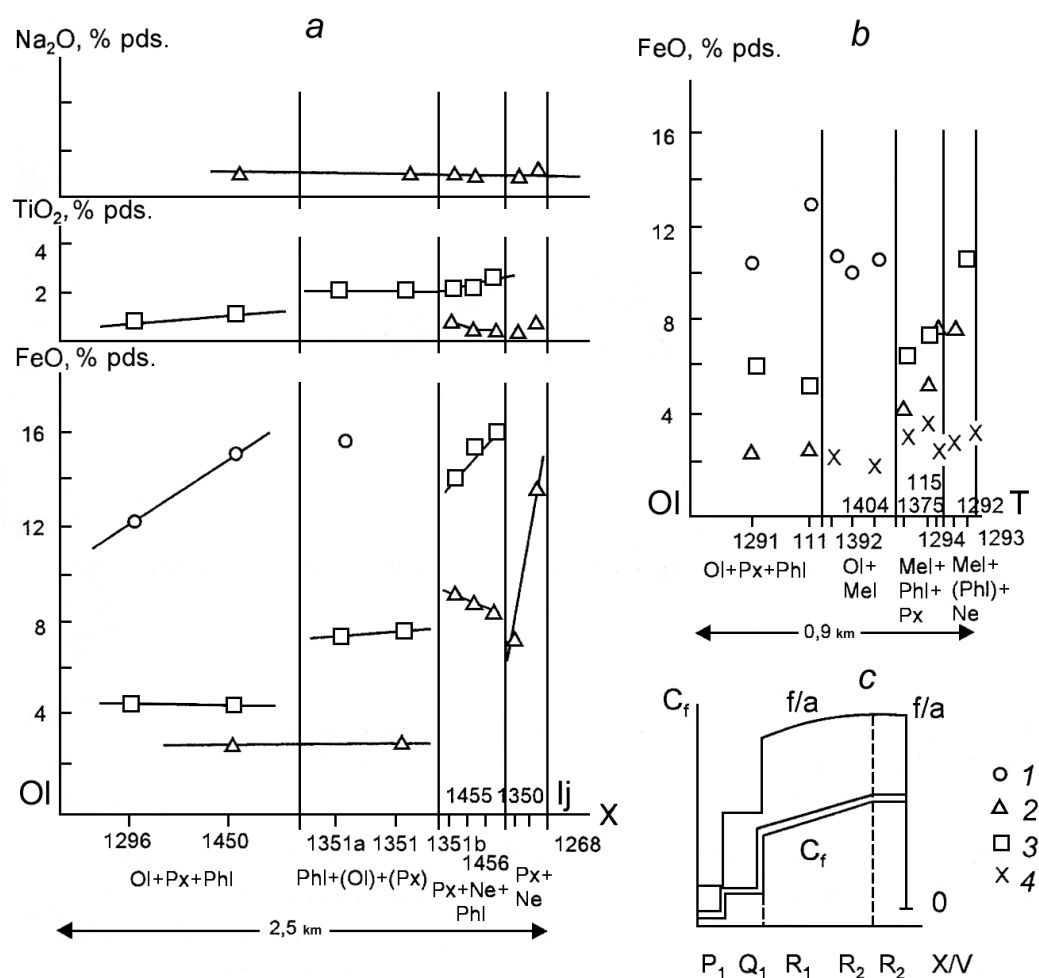


Fig. 15.7. Variation of FeO, TiO_2 , Na_2O concentrations in coexisting olivine (1), pyroxene (2), phlogopite (3), melilite (4) from successive zones of metasomatic columns: a – ijoliteization, b – turiaitization. On the abscissa – position of samples [Rass, 1986] in the cross-sections: olivinite (O) – ijolite (I) and olivinite (O) – turiaite (T); b – diagram of concentration variations C_f of D.S.Korzhinsky [1982] in solution and f/a in rock minerals in function of variation in corresponding distance x/v .

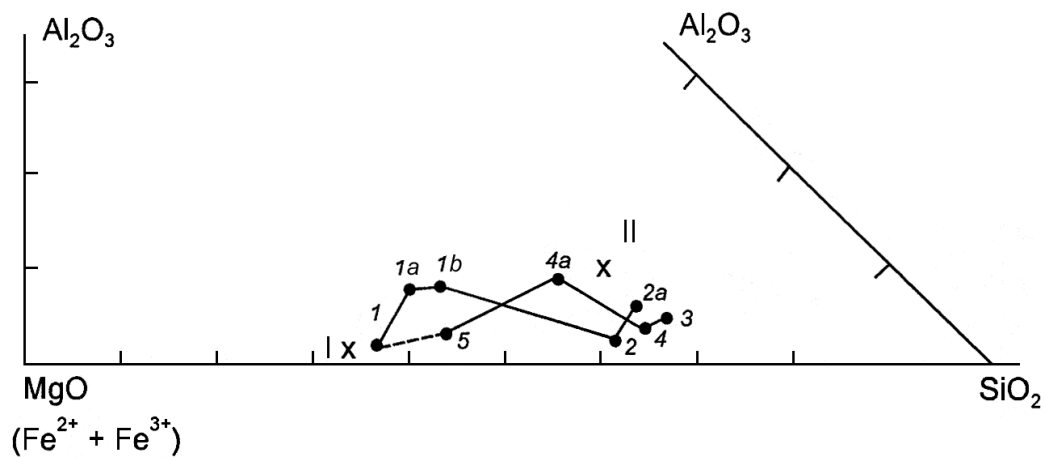


Fig. 15.8. Shift of figurative points of rock compositions – successive zones of metasomatic columns.

1 – phlogopitized olivinite; 1a – pyroxenite olivinite; 1b – glimmerite; 2 – nepheline-pyroxene rock; 3 – nepheline-melilite rock; 4 – phlogopite-melilite rock; 4a – olivine-melilite rock; 5 – melilitolite. Also shown the compositions of olivinites (I) and melteigite-ijolites (II).

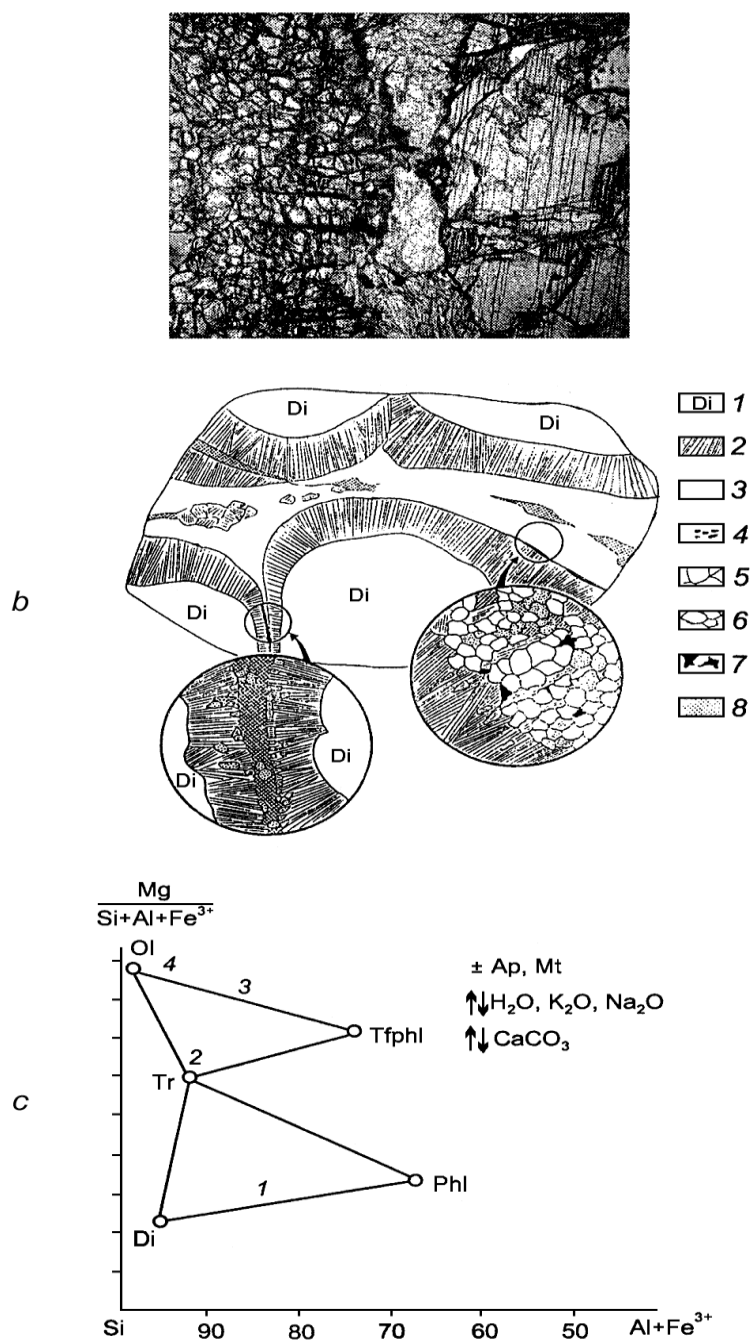


Fig. 15.9. Carbonatization of pyroxene-nepheline rocks.

a – zonal: diopside+phlogopite (tremolite) olivine+apatite+tetraferriphlogopite. Thin-section 5, magnification 20, natural light; b – carbonatite veinlets with reaction zones in coarse-grained diopside rock (sketch of a sample, reduced 2 times); in insert circles – details of the sections; 1 – diopside; 2 – tremolite; 3 – mineral aggregates of olivine, tetraferriphlogopite, apatite; 4 – tetraferriphlogopite; 5 – olivine; 6 – apatite; 7 – magnetite; 8 – calcite; c – diagram of metasomatic parageneses of the phlogopite complex of the Kovdor massif: 1 – 4 – zones of metasomatic column.

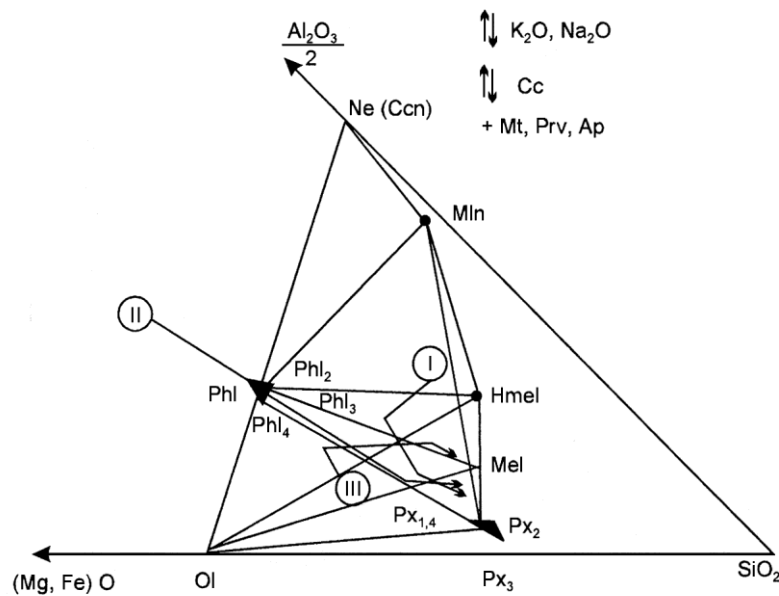


Fig. 15.10 Diagram of facies of postmagmatic metasomatites of the Gulin massif on (I) melteigites and pyroxene- nepheline rocks; (II) olivinite and pyroxene olivinite rocks; (III) melilite rocks.

Ol – olivine; Phl₁ and Px₁ – phlogopite and pyroxene from olivine-pyroxene rocks; Phl₂ and Px₂ – from nepheline-pyroxene rocks; Phl₃ and Px₃ – from melanite-containing pyroxene-nepheline rocks; Phl₄ and Px₄ - from pyroxene-calcite rocks.

CHAPTER 16

Skarns

Definitions. Types of skarns. The term skarn appeared in the literature at the end of the last century from the vocabulary of swedish miners. So they designated ore-containing rocks, formed of calcicium and magnesium silicates and aluminosilicates spreading on deposits of central Sweden. However, the notions of “skarns” and “skarn deposits” were confirmed in the thirties and fourties of our century after the works of P.P.Pilipenko [1939] , D.S.Korzhinsky [1948, 1953] and other known researchers [Abdulayev, 1947 ; Karpova & Ivashentsev, 1954], supplanting terms that were in circulation such as “tectites”, “contact metasomatites”, contact metamorphic, pyrometasomatic deposits. Now [Zharikov, 1968, 1970 ; Economic Geology, 1982], the terms skarns and skarn deposits are generally accepted . More than a century ago, to be sure, were investigated, with the works of B. von Cotta [1864] and A.Groddeck [1876] skarn deposits, the most varied hypotheses were put forward about their genesis : 1) the hydrochemical [I.Lambert, I.Morozevitch & *al*] ; the metamorphic [I.Rosenbush, S.Lead & *al.*] ; 3) the magmatic [E.Fedorov, X.Johannsen & *al.*]; 4) a few variants of the metasomatic and the hydrothermal [A.Zavaritsky, V.Lindgren, V.Goldschmidt, D.S.Korzhinsky, P.P.Pilipenko & *al*]

At the present time, the most commonly admitted proved to be the « contact-reaction » theory of skarn formation advanced by D.S.Korzhinsky [1945, 1948, 1953] and thoroughly elaborated by his successors [Zharikov, 1968, 1985, 1991 ; Zaisky *et al.*1986, 1989 ; Zaisky, 1989] According to present developments, skarns occur as a result of the interaction of carbonatic rocks with magmatic and other aluminosilatic rocks by means of magmatogene solutions. From which follow definition and typization of the skarns.

Skarns are called metasomatic rocks formed of calcicium, magnesium and iron silicates and aluminosilicates, arising in a zone of high-temperature contact aureole of intrusion resulting from interreaction of carbonate rocks with a magma and other aluminosilicate rocks by means of magmatic solutions.

In mineral composition and parageneses are distinguished *magnesian skarns* and *calcic skarns* ; they also differ in conditions of formation and geological setting..

In the mechanism of formation are distinguished *diffusion* skarns (bimetasomatic) and *infiltration* skarns (contact-infiltration and autoreaction skarns).

Finally, depending on the composition of the initial rocks, they differ into *endoskarn* and *periskarn*¹ rocks, which form on aluminosilicate rocks ,and *exoskarns*, formed on carbonate rocks. If carbonate rocks contain initial silicates or aluminosilicate material, the exoskarns are called *skarnoids*. They are distinguished by the presence of numerous minerals (derived from the initial aluminosilicate material) and they do not display a zonal distribution of pyroxene and garnet. Apart from those rocks originated in contact reaction, is distinguished yet another group, the *autoreaction* skarns, arising in calcic metasomatism without a necessary intervention of carbonate rocks. On table 16.1 the optimal subdivision of skarns rocks is adduced in a systematizing aspect

Together with the marked types of skarns generally accepted, some researchers distinguish sometimes also « ferruginous skarns », and relate to them totally different metasomatites. In some cases [Burt, 1974] there are ordinary calcic skarns with strong ferruginous pyroxene and garnet, ilvaite and magnetite. In other cases [Strygina, 1964, 1978], to the skarn are arbitrarily linked totally different metasomatites encountered amid ferruginous

Table 16.1 **Types of skarns**

On mineral composition	On mechanism of formation
Magnesian (MgSk)	Infiltration (inf)
	Contact-infiltration
	Diffusion (dif)
	Bimetasomatic (bim)
Calcic (CaSk)	Infiltration (inf)
	Contact-infiltration
	Autoreaction (auto)
	Diffusion (dif)
	Bimetasomatic (bim)

¹ Are called periskarn rocks (enclosing skarns) formations of endoskarns composed chiefly of feldspars, scapolite and other aluminosilicates, bringing about by desilicification of the initial aluminosilicate rocks.

table (continuation)

On composition of replaced rocks	Typomorphic minerals
Exoskarns	Fo, Cpx, Spl (Per, Mtc, Gel – facies of feeble depth)
Endoskarns, periskarns	Cpx, Spl, Pl, Scp, Kfs
Exoskarns	Cpx, Fo, Dol
Endoskarns, periskarns	Cpx, Phl, Pl, Scp, Kfs
Exoskarns, skarnoïds	Cpx, Grt, Wo
Endoskarns, periskarns	Cpx, Grt, Pl, Ep, Sc, Kfs
Endoskarns, periskarns	Cpx, Grt, Ves, Ep, Pl etc.
Exoskarns, skarnoïds	Cpx, Grt, Wo
Endoskarns, periskarns	Cpx, Grt, Ep, Pl, Sc, Kfs

quartzites or in contact with granitoids and built with almandine, spinel, hypersthene, fayalite. These metasomatites have another origine than ordinary skarns and calling them skarns is pointless. Likewise, one should not called « manganese » skarns rocks occuring in the metamorphism of rich manganous sedimentary volcanogenic masses and built of minerals such as rhodonite, babingtonite, spessartite, etc. Although we must remark that manganous pyroxenes and pyroxenoids : johannsenite, bustamite , rhodonite are hihgly characteristic of skarn polymetallic deposits. Sometimes they have distinguish «alkaline skarns » [Zhao *et al.*,1990] thus underlining the peculiarity of usual contact skarns , occurring in connection with intrusion of alkaline rocks in dolomitic or calcicitic marbles. Their peculiarities, naturally, are expressed in the formation of « sodic minerals »: aegyrine, aegyrine-augite, akermanite, nepheline, sodalite, lazurite, albite, and other «alkaline» minerals. With predominance of those minerals the corresponding rocks must not be called skarns, although their contact-reactional, bimetasomatic genesis, as a rule, makes no doubt.

Geological setting of skarns and skarn deposits. Skarns are widely distributed on the earth crust. However for their origin it is necessary to count at least three indispensable conditions. In the first one, there is presence of contact of two chemical environments in disequilibrium, carbonate rocks and aluminosilicate milieu, which can be represented either by a magmatic solution or an intrusive rock or any other aluminosilicate rocks (gneisses, micaschists, etc.). In the second condition, skarns are formed of high temperature minerals, therefore they always occur in immediate contact with intrusions, or in a zone of high temperature contact aureole of intrusive massifs. Finally, in the third condition, for the flow of intensive processes of contact infiltration or

bimetasomatic skarn formation, participation of hydrothermal² solutions is necessary, usually of magmatogene origin. These symptoms are necessary for all « genuine » skarns. Reduction of whatever factor leads to devolution in skarn-like rocks or in other reaction metasomatites of « non-skarn » genesis.

A clear link between skarns and magmatism renders interesting an evaluation of confined (not only spatially but also of genetically) skarns in different magmatic formations. Such an evaluation (on more than 100 skarn deposits) was made by us [Zharikov, 1968] and is presented on fig. 16.1. Magmatic formations are taken oversimplifiedly (even eclectically, for example formation of small intrusions, in counterpoise of others, on substantial associations of intrusive rocks); however, the geological setting of each formation is completely defined and sufficient for our aims. The figure clearly shows a primary link between skarns and gabbro-syenite-plagiogranite and, especially with granitoid formations, which develop in early and middle stages of the geosynclinal cycle or, in the contemporary terminology, are linked with insular arc and collision (orogene) geodynamic regime.

For a more detailed characteristic of the geological setting of skarns and characteristic mineralization is offered on table 16.2. This table, of course, does not include all the varieties of skarn formations, but reflects the main peculiarities (an enumeration of skarn types reflects only the relation of extension but not genetic succession).

In this table are shown, apart from skarns, the composition of ores developed in the various skarns, which have as is well known, a substantial economic significance. Depending on correspondence of skarn formation processes and mineralization, it is usual to distinguish several types of mineralization or families of skarn ores [Zharikov 1960, 1965, 1968]:

- 1) type of simultaneous mineralization
- 2) type of concomitant mineralization
- 3) type of superimposed mineralization

The type of simultaneous mineralization, where the deposition of the ore minerals occurs during the process of skarn formation, has a very limited extension (we have in mind namely mineralization, but not in significant quantity of, for example, magnetite usual in the outer zones of magnesian skarns). To this type is related the borate mineralization in magnesian skarns, the phlogopite mineralization in magnesian skarns and autoreaction skarns. However in these cases, industrial borates and phlogopites are formed later, at the succeeding recrystallization of the initial skarns, and quite often are accompanied with other apokarnic minerals.

² By hydrothermal solutions, we understand essentially “boiling” aqueous fluids having properties of “liquid” character, independently of their consistency. The source of these fluids (judging by isotopic composition) is of magmatic origine, principally juvenile, although in some cases vadose waters are evidently present.

Table 16.2

Geological position of various types of skarns and ores

Geological setting	Magmatism	Skarns	Mineralization
Old shields	Granitization, granitoids, pegmatites	Mg-Sk (inf, dif) Ca-Sk (inf) rarely	Phlogopite Fe, B (concomitant)
Activation of old shields	Granitoids (mixed series)	Ca-Sk (inf, dif)	Cu, Pb, Zn, Au etc.hers (superimposed)
Platforms	Alkaalino-ultrabasic Trapps	Mg-Ca-Sk (auto) Mg-Sk (inf) Ca-Sk (inf) Mg-Ca-Sk (auto)	Phlogopite Fe, rare grounds, rarely, (concomitant) Fe, polymetals (concomitant)
Earlier stages of geosynclinal development (island-arc regime)	Gabbro plagiogranitic Gabbrosyenitic	Ca-Sk (dif, inf, auto) Mg-Sk (inf)	Fe, Cu, Co, (Au,, polymetals (concomitant and superimposed)
Intermediary stages of geosynclinal development (synorogene regime)	Granitoid (grano-diorite-granitic formation)	Ca-Sk (dif, inf) Mg-Sk (inf)	W, Mo, Sn, Cu, Zn Pb, Be, B (superimposed)
Late stages of geosynclinal development (postrogene and late postrogene regimes)	Formation of feeble intrusions (various formations of granitoids to alkaline rocks)	Cu-Sk (dif, inf) Mg-Sk (inf)	Pb, Zn, Cu, W, Sn, B, Au, Ag and oth. (superimposed)

Nevertheless, are renewed for some time attempts of several researchers [Ezhov, 1994]] to relate part of the magnetite, scheelite and sulfide mineralization immediately to skarn formation. As arguments are utilized facts of discovery of disseminated metallic minerals in association with pyroxenes and garnets. To tell the truth we must remark that on experimentally reproducing bimetasomatic skarn formation, under the influence of solutions, strongly enriched in chlorides of ore elements, principally in contact of marbles with exoskarns, is observed a dissemination of ore minerals : magnetite, sulfides (in the presence of sulfur in the system) ; sometimes magnetite forms a continuous « zone » [Zaraisky & *al.*, 1986 ; Ezhov & Zaraisky, 1994]. If we turn to natural objects, a detailed scrutiny shows that the appearance of ore minerals is always accompanied with change of the initial skarn and, if this mineralization occurs at high temperature, a recrystallization of skarn minerals happens with formation of more ferruginous pyroxene and « ore » garnet (more ferruginous and with greater content of pyrospite molecules). We can be persuaded that the dissemination of those minerals, scheelite-sulfides, tends to be accompanied by silicified skarns. If we now study the opposite geochemical tendencies of skarn and ore process, presentation of a « simultaneous » mineralization of skarns proves implausible.

Ore of the second type,, the family of concomitant ores, is characteristic of various types of skarns. Mineralization of the concomitant type immediately modifies the process of skarn formation and is usually accompanied by a change of the initial skarn minerals. To this family are related magnetite and ludvigite ores of magnesian skarns, phlogopite ores of magnesian and autoreaction skarns, magnetite ores of calcic and autoreaction skarns, magnetite-chalcopyrite and pyrrhotite ores of calcic skarns and a few other ores. This type of ore deposit arises at the earliest postmagmatic stage, which is also the stage of skarn formation, and this is linked with a change in the properties of the solutions at lowering of their temperature and alkalinity.

Finally, the family of superimposed ores brings together ores, arising in interaction of acid solutions at a much later stages (stages of acid leaching) with basic environment of skarns. Mineralization occurs on the front of interaction and is accompanied by peri-ore alterations of skarns, which appear as a favourable environment for ore deposition. To this type are related various ore deposits: scheelite-sulfidic (with SnO_2), scheelite-molybdenite and polysulfidic (often with Au) ores of calcic skarns, polymetallic ores of calcic skarns and many others. Characteristically, each type of mineralization is accompanied, as a rule, by specific metasomatic changes, corresponding to well known formations of periore metasomatites. Skarn mineralization and, accompanying it, metasomatic aposkarnic change represents a facial variety of these processes, issuing preferably for the ore deposition of the main skarn environment.

Therefore the specific skarn mineralization is predetermined by the general character of the occurrence of an acid stage in the given metaliferous field.

As can be seen from what preceeds, skarn deposits are formed as a result of the combination in space of several processes of formation and mineralization of skarns ; moreover this combination reflects a deep genetic regularity of development of one hydrothermal process. We offer table 16.3 in which are shown the main genetic correspondences of the processes of formation and mineralizations of skarns . In the same table, to complete the description, are characteristic markings of temperature, pressure (depth) and main peculiarities of the solutions, based on experimental data, on the research of inclusions, more detailed data to which we refer infra.

As can be seen on the table, at magmatic stage in all the facies of depth there occur contact-infiltration magnesian exoskarns, arising as a result of interaction of dolomites (and other magnesian carbonate rocks) with solutions produced from crystallization of the magma on a front of magmatic replacement of carbonatic rock mass. In conditions of abyssal facies at magmatic stage, outside the front of magmatic replacement, but in the zone of a high temperature aureole, is possible the formation of contact-infiltration and bimetasomatic endo-and exoskarns in contacts of gneisses with dolomites (and other magnesian skarn rocks).

Calcic skarns at magmatic stage do not occur under the influence of instability of calcic silicates in conditions of high pressure of carbon dioxide.

At the early postmagmatic stage, the processes of skarn formation substantially depend upon depth. In conditions of hypabyssal and mesoabyssal facies in contact with alumino-silicate rocks and with limestones and dolomites arise calcic skarns of bimetasomatic and contact-infiltration type. Magnesian skarns in these facies of depth are absent, only sometimes in the outer zone appear calciphyres, formed most probably as remainders of magnesian skarns at magmatic stage, at which are always formed calcic skarns. On the contrary, in conditions of abyssal facies, at early post magmatic stage arise magnesian skarns of contact-infiltration and bimetasomatic type. Calcic skarn formation in abyssal facies conditions are practically absent, to them it is only possible to relate much later garnet,epidote veins in endo- and periskarn rocks.

Table 16.3.

Main genetic properties of formation of mineralizing skarns

Stages	T°C	Facies of depth (h, km ; p ^f)		
Magmatic	650-900	Hypabyssal	Mesoabyssal	Abyssal
		1-3(4) km, p ^f =0,25-1 kbar	3(4)-15(16) km, p ^f =1-3(4) kbar	15(16)-30(40) km, p ^f =3(4)-8(10) kbar
		Mg Sk (inf)	Mg Sk (inf)	Mg Sk (inf, dif)
Earlier postmagmatic (alkaline)	450-750 (800)	Are formed under action of magmatic alkaline fluids with high CO ₂ activity		
		Ca Sk (dif, inf, auto)	Ca Sk (inf, dif, auto)	Mg Sk (inf, dif) Ca-Mg Sk (auto)
	300-500 (600)	Are formed under action of postmagmatic substantially chloridic solution; CO ₂ activity depends upon depth		
Acid	250-500 (550)	Accompanying mineralizing skarns, linked with growth of acidity of chloridic solutions des solutions chlorurées		
		Fe ; Fe-Cu, Fe-Cu-Co, borates, phlogopites	Fe ; Fe-Cu, Fe-Cu, Fe-Cu-Zn, borates	phlogopites borates Fe ; Fe-Zn
		Imposition of mineralizing skarns linked with action of solutions and formation of metasomatites at stage acid leaching		
		1. metasomatism Q+Fsp (W, Mo, Sn, Zn) 2. metasomatism Q+Mc (Sn, Be, B, Mo, W) 3. metasomatism Q+Ep+Chl (Zn, Pb, Cu) 4. metasomatism Q+Ser, Q+Ser+Ank (W, Cu, Mo, Au, Ag, Pb) 5. metasomatisme Q+Tu (B, Zn, Pb) 6. Other types		
		Usually lacking and studied insufficient		

Marked peculiarities of extended magnesian and calcic skarns depend, as we indicate infra, upon the geochemical regime of carbon dioxide, magnesium and calcium in different facies and depth conditions.

Mineralization of concomitant type develops in calcic and magnesian skarns in conditions of regressive evolution of development of the early stage. Usually it is linked with greater basic intrusive complexes and appear as gradual increase of acidity in replacement of initial skarns by ores and aposkarn minerals.

In these conditions, when skarn deposits are linked with acid intrusive complexes, the skarn process of alkaline stage rapidly transform by metasomatic processes of the stage of acid leaching, the formation of which leads to multiform skarn mineralization.

16.1 Magnesian Skarns

Definition. Among skarns, i.e. of high temperature contact-metasomatic rocks, D.S.Korzhinsky proposed to distinguish a type of skarns, characterized by his substantially magnesian composition, calling rocks of this type « magnesian skarns », in contrast to « calcic skarns » characterized by calcium or iron-calcium contents. This delimitation proved important not only for composition but for the genetic peculiarities and the ore's specific character. D.S.Korzhinsky [1953] estimated that in chemical composition, magnesian skarns are even nearer ultrabasic magmatic rocks than to calcic skarns.

We call magnesian skarns high temperature contact-metasomatic rocks arising as magnesian minerals (mainly silicates), and forming in the contact zone of silicate and magnesian carbonate rocks. Typomorphic minerals of magnesian skarns are fassaitic clinopyroxenes, diopside, enstatite, forsterite, humite minerals group, monticellite, merwinite, akermanite, spinel, serendibite, phlogopite, pargasite, clintonite and magnesian borates (ludvigite, warvikite, suanite, kotoite, singalite, fluoborite). They essentially differ from calcic skarns, arising usually as salite-hedenbergite clinopyroxenes, granditic garnets, vesuvianite, epidote and wollastonite. Are proved specific useful minerals of magnesian skarns : phlogopites, magnesian and magnesio-ferruginous borates. Ferruginous and non-ferruginous ores are widely developed in magnesian as well as in calcic skarns.

The first researchers of magnesian skarns were Swedish geologists [Geyer, 1939], who described the mineral deposits of iron ore with boron mineralization of central Sweden, and Watanabe [1943] who studied boron mineralizations and the genesis of contact-metasomatic rocks in North-Korea.

To an elaborate theory of magnesian skarn formation are devoted works of D.S.Korzhinsky [1947, 1953, etc], completed by the study of deposits of Cisbaykal and Aldan in Siberia.

Further, magnesian skarns were minutely described by many researchers [Tilley, 1951 ; Zharikov, 1959, 1968 ; Litsarev, 1961 ; Shmakine, 1961 ; Alexandrov & *al.*, 1968; Pertsev, 1971, 1977 ; Shabinine, 1973, 1974, 1978 ; Shabinine & *al.*, 1984]. A large serie of experimental works concerning the arising of diffusion metasomatic columns of magnesian skarn type was given by G.P.Zaraisky & *al.*[1986].

Geological Setting. Magnesian skarns are expanded in carbonatic (dolomitic) terrains in districts of inversed granitoid magmatism and in regions of tectono-magmatic activation. They occur in aureoles of magmatic bodies and zones of migmatization. In that space are not only skarns on carbonatic rocks, or « exoskarns », but also formations on silicate rocks (developed magmatic or metamorphic), or « endoskarns ». Like other types of contact-metasomatic rocks, magnesian skarns may form bodies immediately in contacts, but also veined and tubular bodies, extending in enclosing rocks on tens or even hundred of meters from the contact. In intercalating patches of silicate and magnesian carbonatic rocks, bodies of magnesian skarns may repeat themselves frequently. Thickness of bodies of magnesian skarns vary from millimeters to tens or a few hundred of meters.

Magnesian skarns of the magmatic stage are formed the earliest. Their geological setting is defined : 1.by the presence in the composition of enclosing rocks of magnesian carbonatic rocks ; 2. by intense magmatic influence, accompanied by magmatic replacement of country rocks. Intrusions may vary in composition from granites to nephelinic syenites and gabbroids, but most typical is their link with granitoid formations (see fig.16.1).

Magnesian skarns at magmatic stage arise at all depths, except the subvolcanic and near surface ones. Formation of these skarns occurs with the following symptoms :

- a) in contact with skarns, the magmatic rocks are not skarnified ;
- b) magnesian skarns intersect apophyses and veins of magmatic rocks, carrying no vestiges of magnesian skarn replacement. As to mechanism, the skarn formation at the magmatic stage is related to the contact-infiltration type.

Structure of of magnesian skarns deposits As cause of the formation of magnesian skarns in high temmperture aureoles of magmatic bodies is revealed a sharp chemical unbalance between magnesian carbonate and silicate rocks or magmas in large intervals of pressure up to a condition of granulitic facies of metamorphism. This unbalance provokes appearance of intermediate chemical compositions of metasomatic zones. We consider this on the typical example of the development of skarns on dolomite at its replacement by a granitic magma. The metasomatic column arising in contact, has the following aspect : granite →

clinopyroxene-bytownite zone spinel-fassaite zone → spinel-forsterite zone → spinel-forsterite-calcite zone (calciphyre) →dolomitic marble. All zones appear simultaneously and expand in the direction of the arrows, and the clinopyroxene-plagioclase zone is immediately replaced by the granite melt.

Formation of any thick skarn zones between granite magma and carbonatic rock is impossible without participation of transmigmatic fluids, i.e. flow of fluids arising through magmatic melts, realizing indispensable matter transport at the formation of skarns. Emergence of skarns as a result of magmatic replacement is marked 1) by the presence of skarn xenoliths in precontact regions of magmatic rocks and magmatic veins in the skarns ; 2) by expansion of all skarn zones aside from the granite, which may be observed either in geological relations or under the microscope owing to incomplete reactions of replacement. Approach of clinopyroxene-plagioclase zones over spinel-clinopyroxene arises as replacement of spinel by basic plagioclases, formation of a plagioclase border around spinel grains. A spinel-pyroxene (fassaite) zone ensues on a spinel-forsterite one, which is reflected, basically, in replacement of forsterite by fassaite on contact of these zones. Reversed correspondences : approach of skarn zones over magmatic rock in these cases is not observed.

The range of magma composition, in which are formed magnesian skarns extends from granitoids to gabbros and dolerites, but also comprises alkaline branches, including nephelinic syenites. In practically all intrusive contacts of these rocks with magnesian carbonatic rocks, one encounters a body of some thickness of magnesian skarn of magmatic stage, proving a high participation of flows of transmigmatic fluids in skarn formation and magmatic replacement of enclosing rocks. Possibly tectonic contacts or rapidly cooling dykes do not contain skarns. Thus, one of the main differences from calcic skarns, are contacts with limestone marbles, in which, with few exceptions, skarns are not formed at a magmatic (progressive) stage. This is shown in the equilibrium of calcite with many magmas in a very wide range of depth at magmatic temperatures. [Pertsev, 1977] Replacement of limestone marbles by magmatic rocks occurs without formation of intermediate reactionzones. So, for instance, the studied cases of " porphyritization" of limestones [Korzhinsky, 1948; Pospelov, 1955]

Magnesian skarns on a progressive stage may form not only immediately in contact with marble, but also in any other contact of silicate rocks with magnesian carbonates in high aureoles of magmatic bodies (or zones of migmatization) under influence of transmigmatic fluids.

We consider cases of skarn development in a stratified patch of rocks, where dolomites alternate with gneisses and a flow of fluids crosses this patch. Forming skarns in dolomites in contact with granitic magmas, the fluids leave in the skarns such components as silica, alumina and get enriched at the same time

with calcium and magnesium. Coming in this way in equilibrium with dolomites, the fluid does not any more produce in them reactions of mineral formation and can only recrystallize the dolomites. However, encountering on their path a further gneiss patch, these fluids prove to be in disequilibrium with the rocks, which initiates replacement of gneisses by endoskarns. Further coming into equilibrium with the gneisses, the fluid ends the formation of skarns, until it meets a new patch of dolomites and so on.

On formation of skarns on silicate rocks the direction of development of the zones will be different. For instance, a spinel-fassaite zone may invade a plagioclase-clinopyroxene one, which is expressed in replacement of plagioclase by spinel and formation of spinel around grains of plagioclase. The skarn formation process with a small quantity of one the reacting surroundings may lead to zoning reduction. Thus, a fine layer of dolomite with full dolomite expansion and prolonged skarn formation process may subsequently lose the zone of spinel-forsterite composition, then that of spinel-clinopyroxene. There may remain only the zone of spinel-plagioclase composition: under intense granitisation this zone also changes into magma, i.e. there occurs a full dolomite granitization. In the opposite case, when a fine layer of gneiss or an inclusion of aluminosilicate rock changes into a skarn, there may remain in the dolomite only a spinel-forsterite skarn.

Together with the infiltrations considered above, is also realized a diffusion mechanism, prevalent in weak fluid flows or in infiltration along the contact. In the formation of magnesian skarns at magmatic stage are prevalent infiltration metasomatic columns. The various successive zones and their mineral composition in the magnesian skarns at magmatic stage depend upon the chemical composition of two reacting surroundings as well as upon external conditions, mainly temperature and depth of formation. As various carbonatic surroundings the most usual are marbles rich in dolomite, magnesite-dolomite marbles, magnesites. The influence of the composition of silicate rocks on the general type of columns are not particularly great. At the passage from quartz-containing rocks to quartzless felspars (for instance syenite, gabbro) from the column vanishes a first endozone (feldspar-pyroxene), it is true, in case of nephelinitic syenites, instead of which appears a zone of nepheline-pyroxene composition [Koniev & Samoilov, 1974]. The most typical column of magnesian skarns was considered above. It is also represented on fig.16.2a. In conditions of less deep formation, and consequently small CO_2 fugacity (as far as CO_2 and depth are linked in straight dependence) and increasing temperature, this usual column is complicated by the appearance of an additional zone of periclase marble (fig.16.2b), which essentially proves not metasomatic, but contact metamorphic. The passage to more common "dolomitic" facies is expressed as dolomitic decarbonatization: $\text{CaMg}(\text{CO}_3)_2 = \text{CaCO}_3 + \text{MgO} + \text{CO}_2$. This facies is usually called "periclase-calcite". It extends rather widely in

the most recent regions with deep skarn formation between 1 and 3 Km [Pertsev, 1977].

In case of skarns developing in contact with basic magmas, i.e. at increasing temperatures in condition of such small depths, there occurs a prolonging alteration of the parageneses. Parts of spinel-pyroxene and spinel-forsterite zones give up their place to spinel-monticellite and melilite zones (fig.16.2c). Prolonged increased temperatures and reduced CO₂ fugacity may lead to formation of rare types of magnesian skarns with merwinites, monticellite-periclase associations, etc. (fig.16.2d).

The succession and composition of zones are also preserved in case of development of magnesian skarns on gneisses, quartzites and similar rocks at a progressive stage; only the direction of the zones development will be different: from dolomitic to silicatic rock. Differences are observed in the chemical composition of the zones. In endoskarns is usually increased the ferruginosity of the mafic minerals, higher content of Zr and Ti and a few other minor inert components, followed by silicate rocks. If magnesian skarns arise on peraluminous quartzites, the frontal zone is plagioclase-cordierite or (under higher temperature) plagioclase-sapphirine. To the cordierite-plagioclase zone follows a biotite-plagioclase or a hypersthene-plagioclase zone (fig.16.3a-c) depending on temperature and chemical activity of K₂O and CaO. More interior endozones (near the carbonatic rocks) may contain clinopyroxene-plagioclase, then spinel-fassaite, spinel-forsterite zones, but in case of magnesian composition of carbonatic rocks, instead of clinopyroxene in the corresponding zones, there is magnesian orthopyroxene. This, however, is characteristic of all exoskarns in contact with magnesites or magnesite-dolomitic marbles. A metasomatic column takes on the aspect represented in fig.16.4a. It is possible, with the skarn formation at low depth in contact with magnesites or brucites between the latter and spinel-forsterite zones of skarns, for a contact metamorphic zone to occur.

Narrowly about to magnesian skarns by way of formation, metasomatic rocks developed in contact not with carbonate rocks but with magnesian silicate rocks of ultrabasic composition. In contact of granitic magmas with dunites, olivinites and serpentinites, there arise zones analogous to magnesian skarns columns, undersaturated in calcium (see fig.16.4b). Examples of such columns are described in the Aldan shield and in other regions [Pertsev & Kulakovsky, 1988; Sack, 1982]. In contact of quartz-containing silicate rocks with ultrabasites there may form analogous columns not as a result of granitisation but with a simple diffusion exchange of magnesium and silica (cf. fig.16.4c).

Alkalinization in the vicinity of contacts. Magnesian skarns at magmatic stage, developed in contact with marble, exert an influence on the chemical and mineral composition of adjacent parts of the magmatic body. Such contact facies are noticeably alkaline enriched. D.S.Korzhinsky [1955] has explained this

appearance of reverse alkaline diffusion toward the magma from the contact with a sharp increase of the activity coefficients of the alkalis on entry of transmagmaic fluids in the basic surrounding, which led to an increase of K_2O and Na_2O chemical activities. There occurs thereupon a difference of activity (or of the chemical potentials) provoking a reverse diffusion reflux of alkalis in the magma. This mechanism is most probable : attempts to explain the given appearance of assimilation of carbonatic rocks have failed since contact facies get enriched in alkalis, but not in CaO and MgO . The existence of magmatic rocks linked with contacts to magnesian skarns is very characteristic. We distinguish, for instance, such pairs : granite + granosyenite, granosyenite + syenite, syenite + nephelinitic syenite. The thickness of alkalinization in endo contact marbles varies from centimeters to tens of meters. Interestingly, in contact with limestone marbles there is no such contact alkalinization. In magmatic massifs adjoining either dolomite or limestone marbles, contact alkalinization is formed only in magnesian contacts [Pertsev, 1971]

Postmagmatic alterations of magnesian skarns at progressive stage. In connection with composition changes of fluids at postmagmatic stage and temperature drop, mineral association in zones arisen at magmatic stage are unstable and exchange place with other associations. Thereupon metasomatism is prolonged, i.e. there is an exchange of components between solutions and solid phases with variation of the chemical composition of the zones. The main parageneses of postmagmatic magnesian skarns are shown on fig.16.5. Postmagmatic alterations of early magnesian skarns are totally usual. They are characterized by the preservation of a few peculiarities of the initial zoning at magmatic stage with deposition of different metasomatic transformations. Postmagmatic metasomatism of early skarns is characterized by appearance of hornblende, pargasite, phlogopite and minerals of the humite group. Alumina-enriched fassaitic pyroxenes are replaced by pyroxene, near to diopside, but free from alumina redistributed in amphiboles and phlogopite. In the zones most rich in silica and alumina, in conditions of small depth, arise calcic skarn associations : wollastonite, wollastonite + grossularitic garnet, vesuvianite, salitic pyroxene.

In (orthopyroxenic) skarns undersaturated in calcium, a postmagmatic transformation also leads to occurrence of phlogopite, pargasite and hornblende instead of spinel-hypersthene and spinel-plagioclase parageneses. In conditions of high pressure, presumably higher than 6 Kbar, postmagmatic transformation of spinel-hypersthene paragenesis, leads to arising of sapphirine in contact minerals.

Magnesian skarns minerals. Minerals composing magnesian skarns have specific properties. Thus there are observed substantial distinctions in homonymous mafic minerals either in various zones of a metasomatic column or in metasomatic columns at magmatic and postmagmatic stage.

Plagioclases in a pyroxene-plagioclase zone at magmatic stage are usually presented in fundamental diversities (from bytownite to anorthite). In same zone of postmagmatic stage, plagioclases are already andesites.

Clinopyroxenes in skarns at progressive stage are rich in alumina; they sometimes contain an increased quantity of titanium. Al_2O_3 concentration in pyroxenes of a clinopyroxene-plagioclase zone is somewhat lower than in pyroxenes of a spinel-pyroxene zone; ferruginosity, on the contrary is somewhat lower in the last. Clinopyroxenes, associated with spinels, appear as fassaitic or near to fassaitic in content of Tschermak molecule. Clinopyroxenes of postmagmatic skarns are distinguished by small content of alumina and titanium and near to the diopside-hedenbergite series. Differently from calcic skarns, they are not highly ferruginous.

Orthopyroxenes are distinguished in ferruginosity, which is higher in association with plagioclases and lower with forsterites (in contact with forsterite zones).

Spinels of magnesian skarns have a comparatively low ferruginosity (up to 30%). In postmagmatic skarns, spinels sometimes contain a noticeable quantity of zinc, up to some weight %.

Olivines of magnesian skarns at progressive stage usually are represented as forsterites. Their ferruginosity does not exceed 12-15% fayalite. In postmagmatic forsterites, it may be rather high, up to 25% fayalite (in association with diopside)

Calcites are encountered in various zones of magnesian skarns. Amongst them are distinguished secondary and early parageneses with skarn minerals. In association with clinopyroxenes they are little magnesian and do not contain exsolution intergrowths, whereas in calciciphyres, in association with initial dolomites, they have a noticeable admixture of magnesium, either isomorphous or in the form of exsolution intergrowths of dolomites.

Amphiboles are formed only at postmagmatic stage. Blue-green skarn hornblendes contain $\text{Al}_2\text{O}_3 = 8.6-15.2 \%$; $(\text{Na}_2\text{O} + \text{K}_2\text{O}) = 2.3-4.3 \%$; $\text{Fe}_2\text{O}_3 = 1.2-4.5 \%$ and $\text{Fe}/(\text{Fe} + \text{Mg})$ from 10 to 55 (mol.). They are often erroneously described as alkaline hornblendes. However, they possess characteristic optical properties with noticeable or strong pleochroism from blue-green on Ng, green on Nm, bright gray-green on Np; $2V = -70^\circ + -80^\circ$, with $\text{Ng} = 19-22^\circ$. Pargasite is characteristic of magnesian skarns. It possesses relatively low ferruginosity ($\text{Fe} / \text{Fe} + \text{Mg}$) from 1 to 35 % (mol).

Phlogopite is wholly typical of postmagmatic magnesian skarns. TiO_2 content in skarn phlogopites is as a rule not high, less than 1 wt. %. In developing on early magnesian skarns, phlogopites are formed in contact with spinel and clinopyroxenes.

Clintonite (xanthophyllite) is found in postmagmatic skarns at small depth and is marked as origin of the passage from magnesian

skarns to calcic skarns. It usually developed in fassaite and spinel zones (or in postmagmatic zones, corresponding to a spinel-fassaite zone on position in the column) and stable in association either with magnesian clinopyroxene or spinel, or with calcic skarn minerals, grossular garnet and vesuvianite, which may develop by replacement of clintonite.

Humites minerals group are formed in magnesian skarns in postmagmatic conditions with increasing fluorinity of fluids. More often than others is found the less fluoric member of the group, clinohumite, after which, in order of diminishing participation, chondrodite, humite and norbergite. Simultaneously may appear two orthosilicates of magnesium : forsterite + clinohumite ; forsterite + chondrodite ; clinohumite + chondrodite ; humite + chondrodite. Ferruginosity in accompanying orthosilicates is various, at the passage of one mineral to another, sharply decreases, in order, forsterite, clinohumite, humite chondrodite, norbergite. Clinohumite may contain increasing TiO_2 quantity (up to 5.4 wt. %), distinguished by a bright yellow coloration and pleochroism. Such Ti-clinohumite may be found in equilibrium with Ti-poor non-colored clinohumites. At postmagmatic formation of new magnesian skarns may sometimes occur two orthosilicate independent zones : calcite-forsterite and calcic-clinohumite or calcic-chondrodite (cf.fig.16.5). At postmagmatic transformation of early magnesian skarns, forsterite at magmatic stage is quite often partially or completely replaced by minerals of the humite group.

There is a specific position in a metasomatic column of minerals of calcic skarns, replacing magnesian skarns, or in postmagmatic magnesian skarns at small depth. So, wollastonite in magnesian skarns always occupies a deep position, representing an extreme endoskarn zone developed on silicate rocks. Wollastonite in strictly calcic skarns always exists in extreme exozone, developing on limestone. Rich grossular garnet develops in magnesian skarns in a pyroxene-plagioclase zone or spinel-pyroxene, i.e. zones rich in alumina. Are particularly easily replaced by grossular garnet thin veins of felspar rocks in magnesian skarns, forming an effect of dissection of magnesian skarns by garnet veinlets. Andradite garnets are formed only in exozones at completion of a skarn process, in oxidizing conditions, and noticeably more rarely than garnets rich in grossular. Vesuvianite, formed in magnesian skarns, after or together with grossular, is according to L.I.Shabinine (1973) MgO rich (more than 2.5 wt. %). Clinopyroxenes, developing together with other calcic skarn minerals, contain no noticeable quantity of alumina and, apart from association with andradite, are poor in oxidized iron ; usually it is diopside-salite. Unlike pyroxene strictly of calcic skarns it is magnesium rich (in calcic skarns is usual ferrosalite up to hedenbergite).

Parageneses of minerals and zoning of magnesian skarns at magmatic stage. To the peculiarity of skarns minerals at magmatic stage are

related : forsterite (fm = 0-15)³, clinopyroxenes (fm = 5-40), spinel (fm = 0-30), calcite, magnetite, plagioclase (in periskarn rocks). In skarns and periskarns rocks of abyssal facies are met orthopyroxenes (fm = 10-45). Skarns of hypabyssal facies are characterized by such exotic abyssophobe minerals as periclase, merwinite, akermanite, monticellite (although some of them are linked with imposition on magnesian skarns of a calcic skarn process).

A noticeable property of clinopyroxene magnesian skarns at magmatic stage is the fact that they are related to fassaites, i.e. to diopsides and salites with increased Al₂O₃ and particularly Fe₂O₃ (together with FeO) content. Al₂O₃ content with fassaites range from 1-2 to 15-16wt.%, with average 4-9wt.%. Correspondingly, Al⁴ ranges from 3 to 20, with average 7-12. Naturally, the greatest alumina content is in paragenesis pyroxene-spinel. At the postmagmatic stage, fassaites « detrude » alumina, changing into usual diopsides and salites.

Coefficients of ferruginosity (f_m) of minerals of magnesian skarns are always inferior to 30 (except that for hypersthene endoskarns fm sometimes reaches 40-50), and the ferruginosity ratio is f_m^{Sp} > f_m^{Cpx} > f_m^{Opx}. Correspondingly, ferruginosity coefficients are less than 1.

For K_{Fe/Mg}^{Opx} = 0.2-0.3, for K_{Fe/Mg}^{Cpx} = 0.3-0.5, for K_{Fe/Mg}^{Sp} = 0.3-0.4.

However, this distribution is fully right only for magnesian skarns..

For other formations with more ferruginous composition arising at another temperature, the distribution of Fe-Mg in the pairs olivine-clinopyroxene and olivine-hypersthene changes. K_{Fe/Mg} increases and takes a value greater than 1. The natural passage is not sufficiently clear. The majority of researchers count that K_{Fe/Mg} for Ol-Cpx and Ol-Opx passes through extremes, which is linked with a non-ideal distribution [P.Ramberg, Kretz, A.A.Marakushev]. Others [Bartolome, D.S.Korzhinsky] suppose that Ol-Cpx and Ol-Opx approach complete mixture, and K_{Fe/Mg} is determined by temperature [Korzhinsky, 1973 ; Zharikov, 1976].

Magnesian skarns are all characterized by various postmagmatic alterations, linked with posterior and other processes, juxtaposed to initial skarns. Amongst them, one may distinguish three groups of minerals. The first consists in minerals linked with regressive alterations and superimposition of a magnesian postmagmatic skarn process. This group is characterized by phlogopite, minerals of the humite group, pargasite, serpentine, minerals of the chlorite group, hornblendes, scapolite. A second group of minerals is linked with a juxtaposed calcic skarn process. This is calcic garnets and pyroxenes, vesuvianite, clinozoisite, scapolite. In conditions of hypabyssal facies with

$$^3 f_m - \text{Fe content} = \frac{\text{Fe}}{\sum \text{Fe} + \text{Mg} + \text{Mn}} \times 100.$$

$$^4 \text{al} - \text{Al content} = \frac{\text{Al}}{[\text{Si} + \text{Al}] + [\text{Mg} + \text{Fe}^{2+} + \text{Fe}^{3+} + \text{Al}]} \times 100.$$

alteration of magnesian skarns and superposition of calcic skarn process there develops a complex of very varied calcium-magnesium silicates : xanthophyllite, monticellite, gehlenite, spurrite and other sparse minerals. Finally, must be noted mineral associations, linked with postmagmatic mineralization of magnesian skarns : magnetites, phlogopites and borates, with moreover, the last, linked with their original complexes of minerals, including also minerals such as ludvigite, suanite, kotoite, fluoborite, szaibelyite and others [Pertsev, 1971].

Parageneses of minerals and zoning of magnesian skarns at magmatic stage are determined by two main factors. First of all fugacity or, more precisely, activity of CO_2 , which in turn directly depends upon depth, significantly extended at pressure increase. Moreover, on parageneses of magnesian skarns appears a relative activity of calcium and iron.

On fig 16.6 is represented a T-P diagram of equilibrated, limited facies of depth of magnesian skarns. The diagram is based on experimental data [Zharikov & *al.* 1977 ; Zharikov, 1968, 1985 ; Walter & Helgeson, 1980] but constructed for an optimal fluid regime at magmatic stage ($\text{XCO}_2 = 0.6$ and $\text{XH}_2\text{O} = 0.4$). For these conditions are plotted stroke-point lines of solidus of granites and basalts. We distinguish four main facies of depth (more precisely T and P, although P has a far more important significance). I merwinite, II monticellite, III periclase, IV non- periclase. The facies are meant on « critical » minerals. The last facies, of course, would be better called forsterite-diopside-spinel, but this paragenesis is also stable in periclase facies. For each facies are constructed diagrams of composition-paragenesis in CaO-MgO-SiO_2 coordinates, reflecting in greater relief parageneses alteration depending on CO_2 fugacity. The first three fields, I-III, reflect a condition of hypabyssal facies which, as we have noted, are characterized by an ensemble of relatively sharp Ca-Mg minerals : merwinite, akermanite, monticellite, periclase. Apart from those attested in the limits of I and II fields, other substances are also possible with parageneses, for exemple Fo + Cc together with Per + Mtc or Per + Ap together with Mtc + Di, , but their field are very small in comparison with those indicated on fig.16.6. We observe (as is well visible on the diagram) that the greatest range of depth contains the non-periclase facies IV : Fo + Di + Cc, which accordingly, is also the most extended amongst skarns at magmatic stage. At this stage are observed the typical parageneses in $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ coordinates. Finally, on the diagram is indicated for comparison the field V, of postmagmatic magnesian skarns, spreading in conditions of abyssal facies and distinguished in parageneses with phlogopite.

Apart from the considered dependence upon depth, parageneses of magnesian skarns and types of zoning in them are also distinguished in their dependence upon chemical potentials of calcium and iron in non-magnetite associations. Here the main difference consists in the appearance of

orthopyroxenes in conditions of low μ_{CaO} . On fig.16.7 is represented a diagram of dependence of parageneses of magnesian skarns at magmatic stage upon chemical potentials of calcium and iron. On the diagram are indicated in Roman digits (I-V) the signs of different facies and dependences upon μ_{Ca} and μ_{Fe} , for which are given diagrams of composition-paragenesis in Mg-Al-Si coordinates. Are also plotted lines of ferruginosity of coexisting Ol-Opx-Spl.

On the diagram are well visible two main groups of facies : non-hypersthenic (fields I and V) and hypersthenic (fields II, III and IV). The main reaction limiting them $(\text{Pl})(\text{Spl}) (\text{Cpx} + \text{Ol} = \text{Opx} + (\text{Ca}))$ practically depends upon the chemical potential of calcium. As far as in the diagram's reckoning the real compositions of the minerals are taken, in the reaction are present spinel or plagioclase (owing to preservation of alumina and fassaite), and the lines of equilibrium have a small slope owing to the sharp ferruginosity of the minerals. From the parageneses marked on the diagram a Fo + Pl association is not found in magnesian skarns, their parageneses answer to fields I, II and III. Moreover,

if the paragenesis of field I $\text{Ol} + \text{Cpx} + \text{Spl}$ is characteristic of depth levels, parageneses with Opx (fields II and III) are met only in conditions of abyssal facies and chiefly in contact with magnetitic masses. These properties are undoubtedly linked with the geochemical regime of calcium in skarn-formed solutions.

The following main types of metasomatic columns are the most spread in magnesian skarns at magmatic stage :

1. magma – Cpx + Spl – Ol(Fo) + Spl + Per – Dol ;
2. magma – Cpx + Spl – Cpx + OL = Spl – Ol + Spl + Cc – Ol + Spl + Dol (Per) + Cc – Dol ;
3. magma – Cpx + Pl(Scp) – Cpx + Spl – Fo + Spl – Fo + Spl + Dol - Dol .

In the outer zones, fronts of magmatic replacements as a result of reaction of interaction of dolomites with gneisses and crystalline schists in abyssal conditions, arise bimetasomatic skarns with characteristic zoning : gneiss (crystalline schists) – Cpx + Pl – Cpx – calciciphire – Dol.

For contact – infiltration endoskarns arising under the influence of magmatogene solutions, on schists or gneisses , which arise in them through dolomites, the following zoning is observed :

Gneiss – Cpx + Pl (Scp) – Cpx + Spl (Phl) – Dol.

Parageneses and zoning of skarns at postmagmatic stage.

Postmagmatic magnesian skarns are reliably studied only in gneiss complexes of Precambrian. They are formed as a result of contact reaction of dolomites and aluminosilicate rocks by means of a diffusion or infiltration mechanism. The regime of magnesium and calcium and the reactions of skarnification are determined by depth conditions. This is manifested in decisive factors exclusively determining coincidence of magnesian skarns at magmatic stage to

old shields and zones of Precambrian folding with active manifestation of granitoid magmatism. Mineral composition of postmagmatic magnesian skarns is varied. We may distinguish two main mineral associations : a) strictly post magmatic skarns and b) postmagmatic replacements of earlier formations (preferentially at magmatic stage) of magnesian skarns.

To the main minerals of strictly postmagmatic skarns are related olivine (forsterite), clinopyroxenes, spinel, phlogopite, hornblende (usually pargasite), plagioclase, scapolite, orthoclase, calcite, apatite. In determined conditions arise lazurite, hauyne, nepheline. Unlike skarns at magmatic stage, postmagmatic clinopyroxenes are usually diopsides and salites (Al₂O₃ content does not exceed 1-2wt.%). Usual range of ferruginosity (fm) of minerals : clinopyroxenes (0-54), olivine (0-20), spinel (4-40), phlogopite (0-30), pargasite (10-35). There is a characteristically great ferruginosity in endoskarns and periskarns. Scapolites have an average 40-60% content of meionite molecules, plagioclases contain 20-30% of anorthite.

Mineral association of altered magnesian skarns is very varied. The most characteristic minerals are chondrodite, humite, clinohumite, phlogopite, amphiboles, chlorites, serpentine, talc, calcite, borates, magnetite, apatite. In conditions of hypabyssal facies in replaced magnesian skarns are also found monticellite, clintonite, brucite and other abyssophobe magnesian and calcicio-magnesian minerals.

Parageneses and zoning of postmagmatic magnesian skarns are also very varied. Paragenetic analysis shows that a determined significance of their formation, apart from the depth condition, has a regime of alkalinity and ferruginosity. Here are the following facies of alkalinity and ferruginosity: a) pyroxene-spinel facies arising in conditions of low alkalinity and ferruginosity ; b) spinel-pargasite facies, arising in conditions of increasing ferruginosity and non-high alkalinity ; c) phlogopite facies, distinguished by moderate alkalinity and low ferruginosity ; d) phlogopite-pargasite facies in conditions of increased ferruginosity and normal alkalinity.

Metasomatic zoning arises under the consequence of reaction interplay of inert components (Si, Al, Mg) under the influence of high temperature metasomatic solutions. Zonation peculiarity is then determined by activity of interacting inert components, the mechanism of their mixing, the general regime of postmagmatic solutions, their alkalinity and ferruginosity.

We distinguish, corresponding to the separate facies, the following main types of metasomatic columns of postmagmatic bimetasomatic magnesian skarns :

1. Gneiss, crystalline schists – Cpx + Pl(Klf) + Scp → Cpx + Scp → Cpx + Spl → Cpx → Fo + Cc + Dol.
2. Gneiss – Cpx + Pl(Klf) + Scp → Cpx + Scp → Cpx + Prg → Cpx + Spl → Cpx + Fo + Cc → Dol.

3. Gneiss $\rightarrow$ Cpx + Pl(Klf) + Scp $\rightarrow$ Cpx + Scp $\rightarrow$ Cpx + Phl $\rightarrow$ Phl $\rightarrow$ Cpx $\rightarrow$ Fo + Cc $\rightarrow$ Dol.

Contact-infiltration skarns are characterized by the same types of zonality

The main lines of chemistry are the following. Formation of exoskarns zones is brought about by introduction of silica and removal of magnesium and calcium, but at the formation of endoskarns there occurs introduction of magnesium and calcium and removal of silica. Moreover alumina is limited to local mixings only within endoskarns. No removal of alumina occurs in exozones. Such postmagmatic magnesian skarns substantially differ from skarns at magmatic stage. Activity of alkalis and iron is determined, chiefly by influencing solutions and turn out, probably as peculiarities of magmatic sources.

We now consider only parageneses of strictly magnesian skarns formed at postmagmatic stage, not touching on the parageneses of replaced skarns and other formations of contact-reaction. On fig.16.8 is represented a diagram of the dependence of parageneses of postmagmatic magnesian skarns upon the chemical potentials of potassium and iron, more substantially influencing the paragenetic correlation in postmagmatic magnesian skarns. In constructing the diagram the following compositions of minerals have been taken : Scp₆₀, Pl₄₀, Prg₂₅, Sp₃₅, Di₂₀, Fo₁₀ (where have been marked by indexes the contents of meionitic and anorthitic molecules and the ferruginosity of Fe-Mg minerals). This diagram characterizes parageneses of all main contact-reaction phlogopitic deposits. It is possible to distinguish the domains of parageneses of low alkalinity and ferruginosity (II, III) without pargasite and phlogopite (phlogopite appears in these parageneses with following replacements of the initial skarn minerals)⁵. Facies of increasing ferruginosity are characterized by parageneses with pargasites (III, IV). Finally, the domains of normal and increasing alkalinity occupy the phlogopite facies V-IX). The mentioned phases are formed simultaneously, i.e. in conditions varying in ferruginosity and alkalinity. At the same time we observe a definite tendency of ferruginosity growth in the course of skarn process, when phlogopite facies are replaced by phlogopite-pargasite.

The diagram may be widened to the domain of high alkalinity and the different correlations of chemical potentials of calcium and potassium. In these conditions arise contact-reaction formations with nepheline, lazurite, hauyne. The classic description of these deposits was made by D.S.Korzinsky [1948]. However, they do not relate to skarns, although their contact-reaction, bimetasomatic nature in the mechanism of formation is completely similar to the nature of bimetasomatic skarn deposits.

⁵ In all parageneses, exploitable phlogopite appears almost ever later during recrystallization and replacement of the skarn minerals.

Alteration of magnesian skarns. With the temperature decrease of postmagmatic solutions, percolating through magnesian skarns, there occur exchange reactions between the minerals of the rocks and the solutions, as a result of which the skarns change their composition. Spinel-forsterite skarns are then transformed into clinohumite or chondrodite rocks with a certain quantity of phlogopite, but spinel-fassaite skarns are transformed into phlogopite more rarely pargasite skarns. Pyroxene-plagioclase periskarn rocks are transformed into hornblende, phlogopite, sometimes tourmaline rocks. Sometimes plagioclase is replaced by scapolite. All these skarn transformations occur without alteration, preservation of the inert components in the rocks, and the processes prove . metasomatic column arises, although the mineral composition of the zones of the initial column is changing.

Fairly frequently are magnesian skarns subjected to replacement by calcic skarns. These skarns are widely combined with bodies of magnesian skarns and develop with replacement of the latter, absorbing simultaneously parts of adjacent active intrusions and hornfelses intercalations.

Periskarn rocks are formed with pyroxene and one of the feldspars, basic plagioclase or orthoclase ; sometimes is formed instead of them scapolite, i.e. the mineral composition of the rocks of this zone of endocontact is close to the composition of periskarn rocks of normal calcic skarns. In them are spread wollastonite, grossular garnets and pyroxenes of the diopside-hedenbergite series.

Contrariwise, skarns of exocontact have a series of differences from skarns formed on limestones . These zones of apomagnesian calcic skarns are characterized by clinopyroxene of salite-augite type, essentially magnesian vesuvianite, grossular garnet, xanthophyllite and rarely gehlenite. These highly aluminous minerals develop with exchange of spinel and basic plagioclase of magnesian skarns, i.e. they sharply distinguish apomagnesian calcic skarns from the usually non-aluminiferous skarns formed on limestone.

Thus, in rocks of magnesian skarn formation spatially coexist groups of high temperature mineral associations : 1) magnesian skarns at magmatic stage (fassaite, forsterite, spinel, basic plagioclase, periclase); 2) post magmatic transformations of magnesian skarns (phlogopite, pargasite, anthophyllite, tremolite) ; 3) apomagnesian calcic skarns (salite-augite or ferrosalite up to hedenbergite, monticellite, xanthophyllite, vesuvianite , grossular, wollastonite). Moreover, in the last group predominate minerals essentially magnesian and aluminous, unusual in skarns formed on pure limestone.

Mineralizations of magnesian skarns. The most usual mineralization of magnesian skarns is magnetite or borates, also other other types are found of skarn metals ores (W, Sr, Mo, Cu, Zn, Pb, Ag, Au).The most important non-metallic raw material in magnesian skarns is phlogopite. Magnetite and borate ores, as well as phlogopite, deposit in a postmagmatic process, but also at the time of formation and transformation of skarns.

Magnetite, primary borates and phlogopites are in equilibrium with skarn zones combined with them and, consequently, are formed at high temperature, even to the stage of hydrothermal alteration of skarns. The remaining types of metallic ores, on the contrary, as in calcic skarns, are linked with acid hydrothermal alterations, precipitating after the passage of the « acid wave ».

Iron ores, magnetite rich, occupy in magnesian skarns a definite position : they are formed most often in a forsterite zone, almost wholly replacing its minerals. Somewhat more rarely do they appear in a clino- or an orthopyroxene zone, where the olivine zone may be oreless. It has been noted [Pertsev & Kulakovsky,1988] that in the development of magnetite in a pyroxene, olivine ferruginosity in an oreless olivine zone is high, reaching 15-17 % Fa. A more basic and more acid surrounding, conditioned by the presence of weak forsterite ferruginosity, was favorable to magnetite precipitation. Magnetite may be stable in any zone of skarns and in surrounding rocks, but it forms rich ores only in replacement of a forsterite or more rarely of a diopside zone. Interstitial development, similar to sideronitic, of magnetite in ores with replacement of such postmagmatic minerals as phlogopite, pargasite, minerals of the humite group, gives evidence about postmagmatic and epigenetic magnetite formation

Of another character is the magnetite mineralization in calcic skarns. In ore composition are present, apart from magnetite, andradite garnet, ferrous epidote, clinopyroxene rich in oxidized iron (ferriaugite), sometimes very rich in marialite scapolite, is found a ferrous blue-green hornblende.

Borates ores are displayed as magnesian borates : kotoite, suanite and Mg-Fe borates of the ludvigite group. In industrial quantities may exist aqueous borate szaibeleite (ascharite), proving a product of low temperature decay of initial skarn borates mentioned above. In industrial quantities may probably also be found carbonate-borate groups of sakhaite, charkerite and kurtshatovite, characteristic of magnesian skarn at low depth [Pertsev,1971]. Borate mineralization occupies a characteristic position in skarns, that is an extreme spinel-forsterite (clinohumite, chondrodite) zone and / or calciciphyre, including formation of monomineral (or nearly so) borate ores. Thin kotoitic mineralization only occurs by means of replacement of magnesian carbomates (or magnesium oxides) in the form of kotoite marble (on dolomite) or kotoite ore on magnesite or periclase. Suanite ore may be formed either by substitution of calciciphyre or forsterite, sometimes also pyroxene zones.

Concentrations of accumulation of ludvigite usually confined to a forsterite zone. Kotoite mineralization is specific to a condition of small depth, not more than 2-3 Km.

Phlogopite raw materials. Although phlogopite mineralization characterizes all magnesian skarns, coarse-leaved industrial phlogopite is characterized only by deep deposits. Moreover it is established that industrial

phlogopite is formed at recrystallization of fine-grained phlogopite [Murzaiev, 1974]. More than that, all minerals found in association with coarse-leaved phlogopites, also present gigantic crystals. Apparently, the process of formation of coarse crystallized phlogopite is akin to the process of formation of alpine veins. In phlogopite deposits it arises in conditions of protracted thermostatic control in regions of stretching. In conditions of small depth such thermostatic control is unlikely because of the high rate of cooling of the rocks.

Scheelite mineralization of small depth occur at silicification of calcic skarns developed on magnesian skarns, where it is associated with postskarn pyroxenes and garnets. Scheelite of deep deposits is formed together with post skarn replacements of magnesian skarn minerals as well as at acid stage but, as a rule without silicification. It associates with such minerals as serpentine, talc and tremolite.

16.2 Calcic Skarns

Mineral association of calcic skarns is characterized by the compulsory presence of calcic pyroxenes alongside diopside-hedenbergite (or series of diopside-hedenbergite-johannsenite) and calcic garnets alongside grossular-andradite. Moreover, to skarn minerals are related wollastonite, epidotes, more rarely vesuvianite, pyroxenoid of rhodonite type, bustamite, monticellite, gehlenite. To periskarn rocks are usually plagioclases and/or calcite, feldspars, scapolites. Secondary minerals are tremolite-actinolites, chlorites, epidotes, sometimes axinite, usually calcite.

A self-formed complex of minerals is formed in conditions of slight depth with deposit of calcic skarns on magnesian ones. Apart from the usual minerals of skarns, garnets, pyroxene and vesuvianite, are met in those conditions monticellite, melilite (gehlenite), spurrite, cuspidine and other more rare calcic and calcic-magnesian minerals.

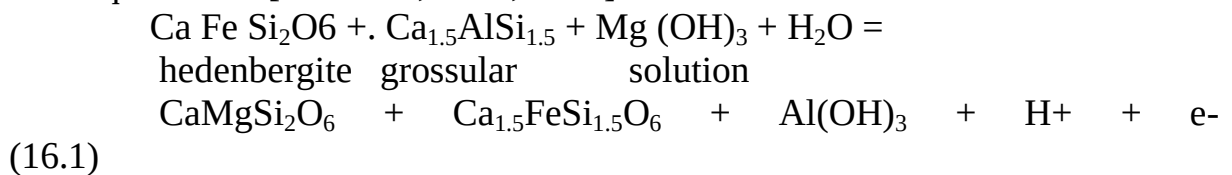
In deposit on calcic skarns of ore processes, a complex of ores and periskarn minerals is highly multiform.

Hundred of analyses of skarn minerals have been published in the literature [Zharikov, 1968 ; Sobolev, 1964 ; Karpova & Ivashentsev, 1954 ; Indikaev, 1980. Einaudi *et al.*, 1981] and it is not possible to enumerate here their results. Most important is the revelation of regular correspondences in composition of minerals of calcic skarns.

We have established [Zharikov, 1968]) that the composition of corresponding pyroxenes and garnets are noticeably distributed in ferruginosity to different skarn deposits. Fig.16.9 shows a comparative diagram, where on the ordinate axis is put $X_{\text{Fe}}^{\text{Cpx}} / 1 - X_{\text{Fe}}^{\text{Cpx}}$, on the absciss axis $X_{\text{Fe}}^{\text{Grt}} / 1 - X_{\text{Fe}}^{\text{Grt}}$. In conformity with earlier publications, the diagram is completed with some new data, the number of which may be greatly increased insofar as a comparison of

ferruginosity of corresponding pyroxenes and garnets has firmly penetrated the practice of skarn research. As can be seen on the diagram, molybdenite skarns, wolfram-molybdenite skarns, tin-wolfram skarns, polymetallic and other skarns are characterized by parageneses of ferrous (hedenbergitic) pyroxenes with aluminous (essentially grossular) garnets. On the contrary, copper-iron skarns, polymetallic skarns are distinguished by reverse correlations : parageneses of more magnesian pyroxenes and more ferrous garnets. Are also widespread with neighbouring correlations ferruginosities of pyroxene and garnet, for exemple in copper-wolfram skarn deposits, sulfide skarn deposits with Au, Co, As and a few others.

Iron distribution between calcic pyroxenes and garnets corresponds with equilibrium [Zharikov, 1966, 1968] :



Diopside Andradite Solution

The constant of distribution is recorded as follow :

$$\frac{[\text{CaFeSi}_2\text{O}_6]}{[\text{Ca Mg Si}_2\text{O}_6]} : \frac{[\text{Ca}_{1.5}\text{Fe Si}_{1.5}]}{[\text{Ca}_{1.5}\text{Al Si}_{1.5}]} = \frac{K_D^0 \cdot [\text{Al(OH)}_3][\text{H}^+][\text{e}^-]}{[\text{Mg(OH)}_2][\text{H}_2\text{O}]} = K$$

(16.2)

where in square brackets are the activities of corresponding components in solid phases and in solution. Taking with approximate activity of alumina hydroxide, magnesium and water as constant but the distributions of minerals between ideal phases, we get :

$$X_{\text{Fe}}^{\text{Cpx}} / 1 - X_{\text{Fe}}^{\text{Cpx}} X_{\text{Fe}}^{\text{Grt}} : X_{\text{Fe}}^{\text{Grt}} / 1 - X_{\text{Fe}}^{\text{Grt}} = K_D^* [\text{H}^+][\text{e}^-] = K_{D^{**}} [\text{H}^+] = K_D$$

(16.3)

Equation (16.3) reflects also our supposition, that the most decisive significance for iron distribution proves to be the acidity of the skarnification solution. In condition of increasing acidity $K_D > 1$, and are characterized parageneses of ferrous pyroxenes with aluminous garnet. On the contrary, in conditions of decreasing acidity $K_D < 1$ and in parageneses with pyroxene are found more ferrous garnets (cf.fig.16.9)

A confirmation of this is seen in the peculiar geological structure of the deposit. Molybdenite-wolframite skarns and other rare metal skarn deposits are linked with leuco-granitoides, processes of skarn formation on them are replaced by mighty processes of silicification, greisenization, quartz feldspathization quartz sericitic metasomatism, accompanied by mineralisation of the skarns All this bears witness to increasing acidity of the solutions, which is also manifest at the skarn stage

However, it was necessary to give a direct confirmation of the influence of the acidity on the remarkable distribution of iron between

pyroxene and garnet . This was obtained as a result of experimental research [Zharikov & al., 1979]. On fig.16.10 is presented a general diagram of dependence of the constant of iron distribution between pyroxene and garnet upon acidity of the solution conforming the correlations (16.2) and (16.3) .

$$\lg K_D = \lg (X_{Fe}^{Cpx} / 1 - X_{Fe}^{Cpx} : X_{Fe}^{Grt} / 1 - X_{Fe}^{Grt}) = \lg K_D + \lg [H+] + \lg (C_{Al} / C_{Mg}) \quad (16.4)$$

for experiments with $P_f = 1\text{ kbar}$, $T = 600, 700^\circ\text{C}$ in the presence of CaCl_2 and HCl solutions of mineral and oxidizing-reduction buffers. As can be seen from correlations (16.3) and (16.4) we have adopted in the experiments the influence on equilibrium of the activities of various soluble forms of Al and Mg, whose concentration ($\lg C_{Al} : C_{Mg}$) was determined by the presence in the experiments of a mineral buffer of olivine + wollastonite + anorthite. It should be noted that the $\lg C_{Al} / C_{Mg}$ value is insignificant and constant [Zharikov *et al.*, 16.3) and can be completely neglected establishing that K_D depends on pH which has besides been done in equation (16.3). In our experiments equilibrium constant K_D included $K_D = K_D^0 \cdot [e^-] / [H_2O]$ (16.5).

K_D^0 depends upon pressure and temperature. Dependence of K_D^0 upon temperature is visible in comparing lines 1 and 2 on the diagram 16.10, decrease of temperature brings about diminution of K_D^0 , combining reaction in the structure of the diopside-andradite paragenesis at lesser temperature. (at lesser entropy)

The influence of redox conditions is visible in comparing line 4 (Ni-NiO buffer) with line 5 (QFM buffer). Increase of activity of the electron (decrease of oxidation potential) leads to an increase of K_D .

However, the most important result of the experiments is the confirmation of the sharply reflected dependence of K_D upon the acidity of the solutions. In all experiments, increase of $\lg [H+] = -\text{pH}$ leads to the increase of K_D and dependence of $\lg K_D$ upon pH is practically linear.

Apart from the examined distribution $\text{Cpx} \rightleftharpoons \text{Grt}$, for the characteristic acidity may be utilized also the coexisting compositions of garnet and plagioclase which, incidentally does not depend upon redox conditions. Not stopping at this detail [Vlassova & Zharikov, 1975], we present a diagram of accompanying compositions of garnet and plagioclase (fig.16.11) for some of the skarns deposits adduced above. It is easily seen that molybdenite-wolframite skarns, wolfram-polymetallic skarns are characterized by parageneses of aluminous garnets with more acid plagioclase ($K_D^{\text{Grt/Pl}} > 1$), while in ferruginous skarns are usual parageneses of garnets, rich in andradite molecule, with more basic plagioclases ($K_D^{\text{Grt/Pl}} < 1$). The constant of exchange reaction may be simply expressed as

$$1 - X_{\text{Adr}}^{\text{Grt}} / X_{\text{Adr}}^{\text{Grt}} : X_{\text{An}}^{\text{Pl}} / 1 - X_{\text{An}}^{\text{Pl}} = K_{D^{**}} [\text{Na}] [\text{H}+]^2 / [\text{Fe}^{3+}] = K_D^{\text{Grt/Pl}}$$

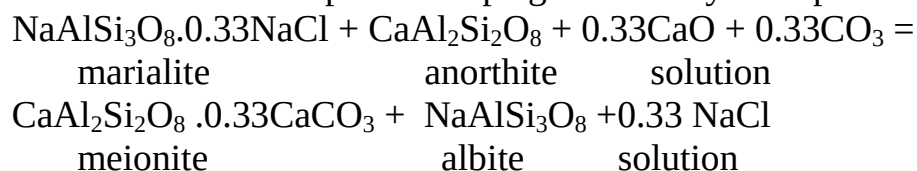
where is evident its dependence upon the acidity of the solutions. The correctness of the decisive influence of acidity on this distribution is seen from

the correlations $K_D^{Grt/Pl}$ and $K_D^{Cpx/Grt}$. On fig 16.12, this correlation is expressed in the form of a graphic $\lg K_D^{Grt/Pl}$ and $\lg K_D^{Cpx/Grt}$ for some skarn deposits represented on fig.16.9 and 16.11. A practically linear dependence between constants confirms the possibility of utilizing them as indexes of acidity of skarn-forming solutions.

Two main conclusions follow from the considered correlations. The first one: the coexisting compositions of clinopyroxene and garnet, garnet and plagioclases may serve as indicator of acidity of postmagmatic solutions, but, insofar as acidity of solutions is a significant measure predetermines the character of the mineralization, coexisting compositions may be utilized to foretell possibly the mineralization of calcic skarns. Another second more general conclusion: component distribution between coexisting mineral metasomatic parageneses depends upon the activity of perfectly mobile components, arising in these minerals and may serve as indicators of activity (chemical potentials) of perfectly mobile components in natural processes.

Let us take one more example of dependence of the composition of coexisting minerals upon the activity of perfectly mobile components having an important significance for understanding the condition of a skarn occurrence.

On fig 16.16 is presented a diagram of coexisting compositions of scapolite and plagioclase for various skarn deposits, contact reaction and metamorphic formations. The exchange reaction of distribution of calcic and sodic end-members between scapolite and plagioclase may be expressed as:



The constant of distribution, reflecting main factors, is expressed in the form:

$$\begin{aligned} X_{\text{Me}}^{\text{Scp}} / (1 - X_{\text{Me}}^{\text{Scp}}) : X_{\text{An}}^{\text{Pl}} / (1 - X_{\text{An}}^{\text{Pl}}) &= K_D^O \cdot [\text{CaO}]^{0.33} [\text{CO}_2]^{0.33} / [\text{NaCl}]^{0.33} \\ &= K_D^* [\text{CO}_2]^{0.33} = K_D^{\text{Scp}} / K_D^{\text{Pl}} \end{aligned} \quad (16.7)$$

where in square brackets CaO and NaCl activities are taken as constant.

From equation 16.7 it follows that, apart from the influence of temperature (K_D^O noticeably depends upon temperature) on the distribution of calcic end-members between scapolites and plagioclases, an important influence indicates activity or fugacity of carbon dioxide. Increase of fugacity (real partial pressure) of carbon dioxide leads to redistribution of calcic end-member from plagioclase and scapolite. As well known, carbon dioxide fugacity substantially depends upon pressure and, consequently, upon depth [Korzhinsky 1949; Shmulovich & al. 1982]; therefore the compositions of coexisting scapolite and plagioclase or constant volume of reaction between their K_D^{Scp} is indicative of depth of formation of corresponding mineral parageneses. As can be seen on the

diagram of fig.16.13, for deep complexes, particularly for Precambrian formations, $K_D > 1$, and parageneses are characterized by more meionitic scapolite with less basic plagioclases. On the contrary, in complexes of middle or small depth, $K_D < 1$, and in paragenesis with plagioclase (usually oligoclase-andesite) are found more acid marialitic scapolites.

An experimental research has been made about the dependence of $K_D^{Scp/Pl}$ upon P_{CO_2} [Kotelnikov,1977]. On fig. 16.14 are presented a few results of the P_{CO_2} = experiments. The main position of line K_D at 500°C for $P_{CO_2} = 0.3$ kbar and 0.4 kbar may show precisely the dependence of $K_D^{Scp/Pl}$ upon pressure of carbon dioxide. On the other side, must be deduced from the diagram a noticeable (reverse) dependence of $K_D^{Scp/Pl}$ upon temperature : temperature increase shifts the equilibrium toward plagioclase. However, for skarn formations of neighbouring temperature (on data in which is also based, in main form, the diagram of fig.16.14), the dependence of K_D^* upon pressure of carbon dioxide and, consequently, upon depth is obvious.

It was interesting to try to evaluate the depth range, answering the change of $K_D^{Scp/Pl}$ from 0.40 to 4.5, if we suppose that it is linked only with change of P_{CO_2} . It is of course only possible to do so approximately. To the change of K_D in 11.25 times ($4.5 / 0.40$) answers the change of P_{CO_2} to 1,533 bar ($\lg P_{CO_2} 11.25 = 0.33 \lg$). If we take a molar proportion of carbon dioxide $X_{CO_2} = 0.2$, the change of fluid pressure amounts to 7,665 bar. Further, taking $P_s = P_f$ and density $\rho = 2.70$, we obtain depth range of 28 Km. If we suppose that fluid pressure is less than lithostatic pressure, the range of depth, answering to the change of K_D from 0.40 to 4.5. For exemple with $P_f = 0.7 P_s$, the change of lithostatic pressure amounts to 10,949 bar, which will answer to a depth change in 40 Km. Of course, all these digits are approximate, it is wonderful that they do not contradict the geological position of the considered prageneses.

Parageneses of calcic skarns are distinguished, grosso modo, according to the temperature of their formation and alkalinity, more precisely, to the importance of the chemical potentials of calcium and sodium in the skarn forming solutions. Apart from that, the composition of the coexisting minerals is indicated by the influence regime of acidity of skarn forming solutions (which has been considered above in detail), redox conditions and exchange of chemical potentials of iron and manganese. Change of depth does not prove noticeably influencing parageneses of calcic skarn (except the examined properties of composition of scapolite and plagioclase), apart from extreme conditions.

First, there is the absence of typical bimetasomatic calcic skarns in abyssal facies of depth. Secondly, manifestation in conditions of particularly small depth and high temperature of calcium rich silicates of the larnite , tilleyite, spurrite types.

Let us first consider facies of calcic skarns in dependence upon temperature and pressure. On fig.16.15 is represented a T-P diagram to which is

experimentally related the study of equilibrium in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ system. Experiments in different parts of this complex system were made by us and other researchers [Zharikov, 1969 ; Zharikov & *al.*, 1977 ; Bulatov, 1974 ; Shmulovitch, 1973, 1975 ; Harker, 1959 ; Harker & Tuttle, 1956 ; Hoshek, 1974 ; Walter, 1963, 1965]]. Some curves have been calculated by us from experimental and thermodynamic data. The diagram presented is not a complete T-P diagram of the system. On it are indicated the separate most important equilibrium curves. Omitted, for example, is a series of experimentally studied curves in the highest temperature parts of the $\text{CaO-MgO-SiO}_2\text{-CO}_2$ system with participation of such rare minerals as spurrite, tilleyite, rankinite. All the experimental curves are established for the condition in which the molar fractions of the fluid's components equal $X_{\text{CO}_2} = 0.2$ and $X_{\text{H}_2\text{O}} = 0.8$. For the characteristic T-P condition of stability of minerals with ferric oxide have been added calculated on thermodynamical and experimental data of equilibrium with participation of andradite, garnet with 40% of andradite molecule and equilibrium $\text{Grt}_{40} \Leftrightarrow \text{Ep}_{20}$. Are also added curves of solidus of granitic and basaltic melts also for the condition $X_{\text{H}_2\text{O}} = 0.8$.

Although each curve delimits the corresponding T- P field, it is expedient to distinguish the following T-P facies of calcic skarns (cf. fig. 16.15) :

- I. Larnite-merwinite
- II. Monticellite-melilite
- III. Wollastonite
- IV. Pyroxene-garnet
- V. Pyroxene-epidote

The larnite-merwinite facies (I) (which naturally may be subdivided into larnite and merwinite subfacies) occurs in conditions of high temperature ($>900^\circ\text{C}$) and small depth, realized in contact with basic intrusions. Typical skarns in these conditions do not occur (garnet unstable) and mineral parageneses characterize the skarnic contact hornfelses with local diffusion fringes.

The monticellite-melilite facies (II), which is also easily subdivided into monticellite and melilite subfacies, represents a high temperature facies of essentially calcic skarns. Temperature range of the facies = $700\text{-}900^\circ\text{C}$. It is characteristic of small and hypabyssal depth. The skarn body combines in contact with basic, intermediate and alkaline intrusions. Together with typomorphic minerals (monticellite, akermanite, gehlenite) are widely spread usual skarn garnets, pyroxenes and wollastonite. On the whole however, skarns of this facies have a limited extension.

On the contrary, the following three facies, wollastonite (III), pyroxene-garnet (IV) and pyroxene-epidote (V) are usually spread skarn facies. Temperature range : wollastonite $600\text{-}700^\circ\text{C}$, pyroxene-garnet $600\text{-}500$ (450) $^\circ\text{C}$, pyroxene-epidote 450 (500) $\text{-}400^\circ\text{C}$. Some garnets and epidote are minerals of

changing composition, passing from pyroxene garnet to pyroxene-epidote facies gradually and stretch in temperature (from 50 to 80°C) then spread intermediate pyroxene-garnet-epidote skarns (in which $f_m^{Grt} > f_m^{Ep}$), and the epidote develops on aluminosilicate rocks. Temperature limits between facies in greater or lesser degree depend upon depth, the digits adduced above correspond to pressure of 1.0 to 1.5 Kbar or depth of 4-6 Km. The determination of temperatures of skarn minerals on gas-liquid inclusions nicely corresponds to these temperature garnets [Zharikov, 1968 ; Indukaiev, 1980].

Let us note also that, unlike lesser deep facies I and II, wollastonite (III) , pyroxene-garnet (IV) and pyroxene-epidote facies occupy a greater range of depth, all the field of existing calcic skarn parageneses, hypabyssal and mesoabyssal facies.

The upper limit of skarn formation occurs in depth of 1.0-1.5 Km, insofar as with lesser pressures high temperature solutions arise in gaseous condition and intense high temperature metasomatic processes of the type of skarn formation are not realized. The lower limit of typical calcic skarn formation, it is expedient to conduct on the line of stability of wollastonite 3.5-4.0kb (crossing the line of solidus of granite), which corresponds to depths of 15-16 Km. Middling in composition and ferruginosity between calcic garnets and pyroxenes stable within all the earth crust, they are also found in conditions of abyssal depth facies.

A variety of parageneses of calcic skarns in significant degree is determined by the regime of alkalino metalliferosity of skarn forming solutions, i.e.depends upon the greatness of chemical potentials of calcium and sodium in skarn forming solutions.

On fig.16.16 is presented a diagram of dependence upon μK and μNa of high temperature parageneses (with wollastonite) of calcic skarns. Insofar as calcium and sodium occur only in composition of feldspars and scapolite, dependence upon alkalinity is reflected in parageneses of periskarn rocks. Initial compositions : $Pl_{50}Sc_{40}Kfs$, Cpx , Grt (of intermediate composition), Wo . To construct the diagram we have taken account of the composition of Scp and feldspars in dependence upon μK and μNa . Owing to this diagram, the line complicates the extreme ext. $Scp \rightleftharpoons Pl + Cpx$ with the extremal correspondences of composition $Pl_{46}Scp_{40}$, $Pl_{41}Scp_{35}$, etc.

In agreement with the diagram it is possible to distinguish the following facies of alkalinity (more precisely metallic alkalinity) of calcic skarns :

1. Pyroxene-plagioclase (or simply plagioclase) facies of normal alkalinity (field I of the diagram). Scapolites are absent in this facies. Usual paragenesis of pyroxene with plagioclase is in the periskarnic rocks.

2. Pyroxene-scapolite (or simply scapolite) facies of increasing alkalinity (increased Na) occupying fields II and III of the diagram. Field II has

a sort of « intermediate » character : it proves to be scapolite, but again stable paragenesis is Cpx + Pl. Field III reflects typical parageneses of scapolite facies.

3. Orthoclase-garnet or orthoclase increased alkalinity (field IV increased mK, and field V increased mK and mNa). Characteristic of the facies is paragenesis of orthoclase with garnet in periskarnic rocks, but in field V, scapolite is found in paragenesis with them.

Parageneses of plagioclase, scapolite and orthoclase facies are usually highly spread in calcic skarns.

Much more rarely are found parageneses of fields VI, VII and VIII, distinguished by the presence of wollastonite with scapolite and/or orthoclase in periskarnic rocks. These are parageneses of high alkalinity, they are well known in some skarn bodies linked with alkaline intrusions.

Alkalinity facies may also be divided similarly for other facies or temperature degrees of the skarn process : pyroxene – garnet and pyroxene – epidote. For the pyroxene garnet, naturally will be absent parageneses of high alkalinity (with wollastonite). Pyroxene – epidote (and intermediate pyroxene-garnet-epidote) are characterized by parageneses of plagioclase-epidote and orthoclase-epidote perior rocks. Facies of alkalinity are usually of the same type for different deposits, skarn fields and even districts. The conditions of alkalinity usually remain uniform at all stages of the skarn process.

A final review of parageneses of alkaline skarns allows us to conclude that they noticeably depend upon the regime of wholly mobile magnesium, manganese and iron. Of general regularity is an increased ferruginosity of all skarn minerals according to the process of flow, from the earlier stages to the last ones, up to the andraditization of exoskarns and deposit of magnetite, which are not skarn minerals any more but are linked with later accompanying processes.

Another peculiarity of some chiefly skarn polymetallic deposits consists in wide expansion of manganese silicates : mixed pyroxenes of the diopside-hedenbergite-johannsenite series (mangano-salites, mangano-hedenbergites), bustamite, rhodonite. They are particularly characteristic of «vein-like » contact-infiltration skarn polymetallic deposits (skarn « pipes » of Karamazar, Dalnegorsk, Trepchi, state of New Mexico and other districts.

Correlations of magnesian and calcic skarns. We have remarked above the peculiarity of extension of magnesian and calcic skarns in their dependence upon stages of the process and the condition of depth. These peculiarities, to repeat them once again, consist in the fact that at magmatic stage on all levels of depth on dolomites and other magnesian carbonatic rocks (magnetite masses and others) are formed magnesian skarns. Calcic skarns in these conditions do not exist. Limestones recrystallize in calcic marbles. At postmagmatic stage, the type of skarn formation depends upon depth. In abyssal conditions in contact with magnesian carbonatic rocks (dolomites, magnesites)

appear magnesian skarns. Typical calcic skarns do not occur in these conditions. Elsewhere, in endoskarn zones appear veins of ferrous clinopyroxenes and garnets, depositing on magnesian skarns. In hypabyssal conditions of depth at postmagmatic stage and on limestones and dolomites are formed calcic skarns. Typical magnesian skarns do not occur in these conditions. Elsewhere on dolomites (with admixture of silica, clayed matter) in the lower zone of the calcic skarns arise calciciphyres.

The mentioned peculiarities of expansion of skarns are determined by the activity (fugacity) of carbon dioxide, by the activities of magnesium, of calcium and by the acidity of the solution. The diagrams on fig 10.3 and 10.12 show the influence of the activity of carbon dioxide. Here we give the results of our [Zharikov & Khodorevskaya, 1987] experimental study of the dependence of skarn parageneses upon a_{MgCl_2} , a_{CaCl_2} , a_{HCl} . An attempt was made to study boundary reactions between calcic and magnesian skarns: grossular $\Leftrightarrow$ forsterite + spinel, and grossular $\Leftrightarrow$ diopside + spinel in the range of $P = 1-3$ Kb at 700°C in reasonable HCl concentrations (10^{-1} - 10^{-3}). However, it appeared that in all those attempts, with variable CaCl_2 , MgCl_2 and HCl concentrations, between the field of grossular and magnesian parageneses (Fo + Sp, Di + Sp) a field of stability is displayed, « intermediary » in composition, of the mineral clintonite. Indeed, these correlations completely correspond to the natural observations, which show that deposition of calcic skarns on magnesian ones always precede a replacement of magnesian skarns with such minerals as clintonite, vesuvianite and phlogopite.

Nevertheless, experimental data characterize the principal correlations between calcic and magnesian skarns in dependence of CaCl_2 , MgCl_2 concentrations (activities) and acidity of the solution. On fig. 16.17 is given an experimental diagram of dependence of equilibria: garnet $\square$ diopside + clintonite, garnet $\square$ diopside + anorthite, clintonite $\square$ forsterite + spinel, clintonite $\square$ diopside + spinel upon CaCl_2 and MgCl_2 concentration in the solutions with various acidity ($m\text{HCl} = 0.1\text{M}$ and $m\text{HCl} = 0.02\text{M}$). The calculated dotted line represents the diopside $\square$ forsterite equilibrium. There chiefly follows from the diagram, that increase in CaCl_2 activity produces a replacement of the magnesian parageneses by the calcic ones, and an equilibrated CaCl_2 concentration on full order, an order higher than MgCl_2 . Acidity decrease shifts the equilibrium in the field of lesser significance of equilibrated CaCl_2 and MgCl_2 concentrations.

Thus, the mentioned geological properties of the formation of magnesian and calcic skarns are determined by the following factors:

1. At high pressure of carbon dioxide at magmatic stage ($X_{\text{CO}_2} > 0.6$) and abyssal facies of depth, impeding the occurrence in these conditions of calcic silicates and aluminosilicates (grossular, wollastonite and specially, high calcic minerals: larnite, spurrite, tilleyite).

2. At low pressure of carbon dioxide and high activity of calcium at the postmagmatic stage and in hypabyssal and mesoabyssal conditions, favorable to the occurrence of calcic skarns and their replacement by magnesian skarns, where they were formed at the magmatic stage.

3. To skarn formation is favorable a low acidity of the skarn forming solutions, on which depends the formation of skarns at magmatic and early postmagmatic stage.

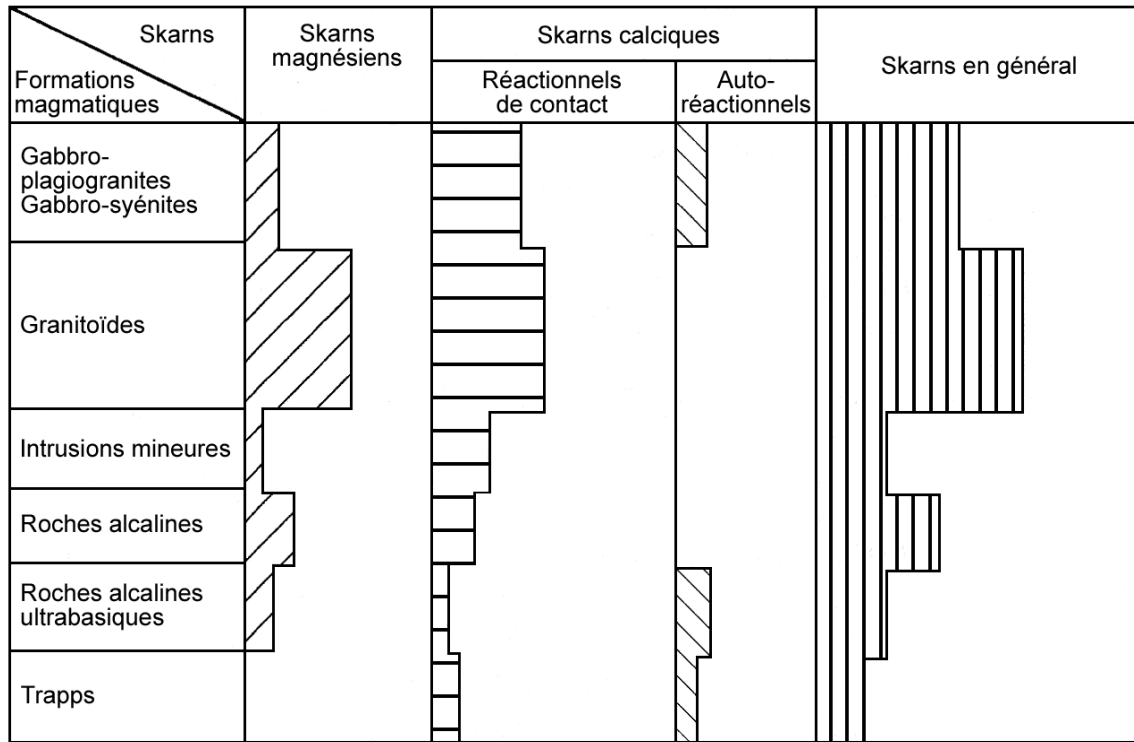


Fig. 16.1. Histogram characterizing confinement of skarns to various magmatic formations (on 120 deposits).

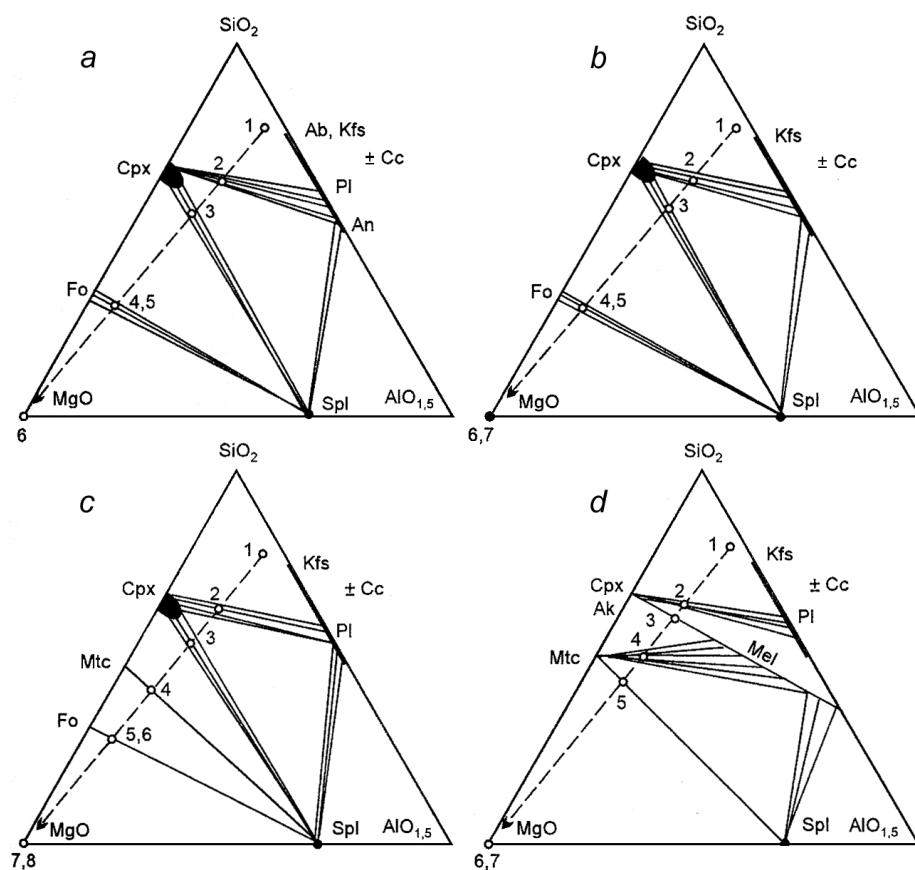


Fig. 16.2. Diagrams of composition-paragenesis for different facies of magnesian skarns of progressive stage.

a – moderate – great depths (dolomite); *b* – small depths (periclase); *c* – small depths and increasing temperatures (monticellite); *d* – small depths and high temperatures (melilite).

Hatched line with arrow indicates tendencies to change of composition in metasomatic columns. Unbroken circles with digits indicate compositions of reacting rocks and metasomatic zones formed between them.

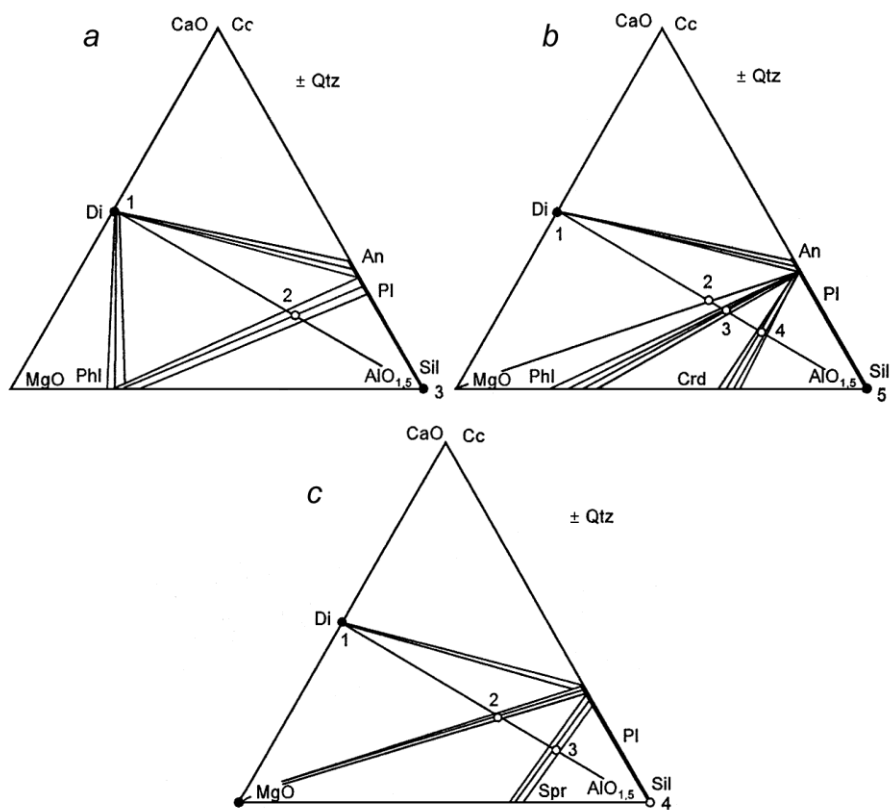


Fig. 16.3. Diagrams of composition-paragenesis of facies of magnesian skarns of dolomite – peraluminous quartzite contacts.
a – biotite ; *b* – cordierite; *c* – sapphirine.

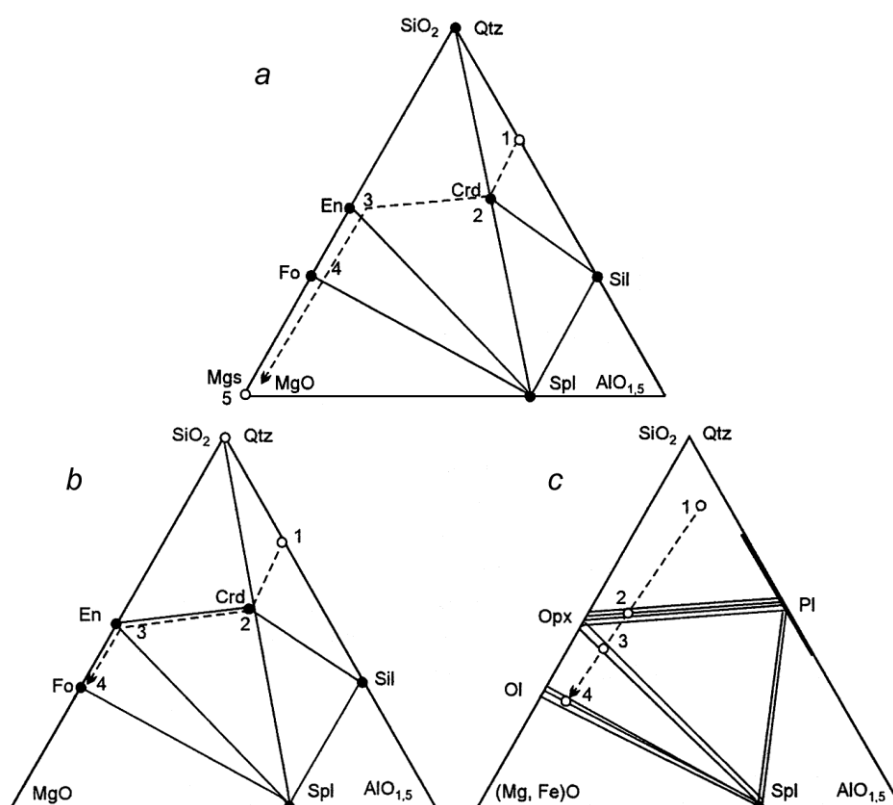


Fig. 16.4. Diagrams of composition-paragenesis of magnesian skarns facies

a – hypersthene – cordierite on magnesite ; *b* – hypersthene on olivinite; *c* – hypersthene on contact olivinite and gneiss.

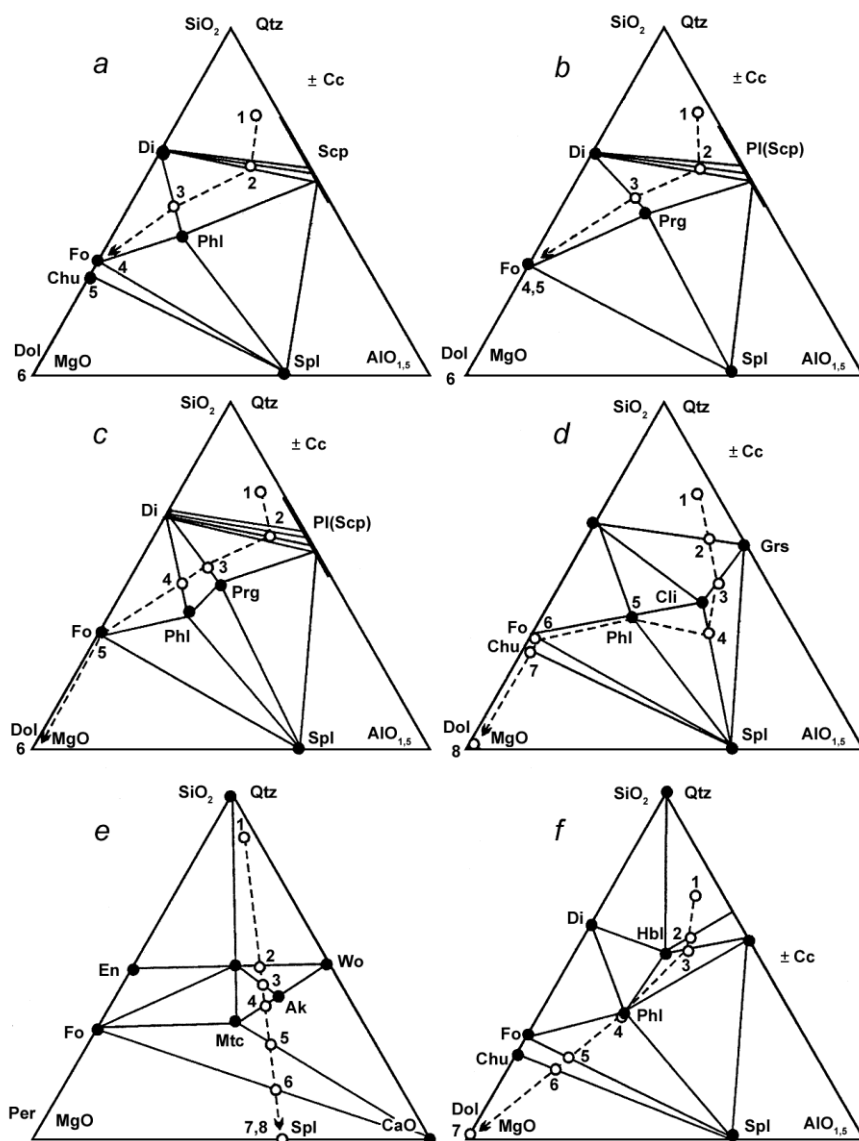


Fig. 16.5. Diagrams of composition-paragenesis for some most typical postmagmatic (regressive) facies of magnesian skarns.

a - c - facies of great depths: *a* - phlogopite; *b* - pargasite; *c* - phlogopite-pargasite; *d - f* - facies of small depths: *d* - clintonite-spinel; *e* - wollastonite -diopside; *f* -hornblende-grossularite. Tendencies to change of compositions, to composition of zones of metasomatic columns and symbols of minerals, as on fig.16.2.

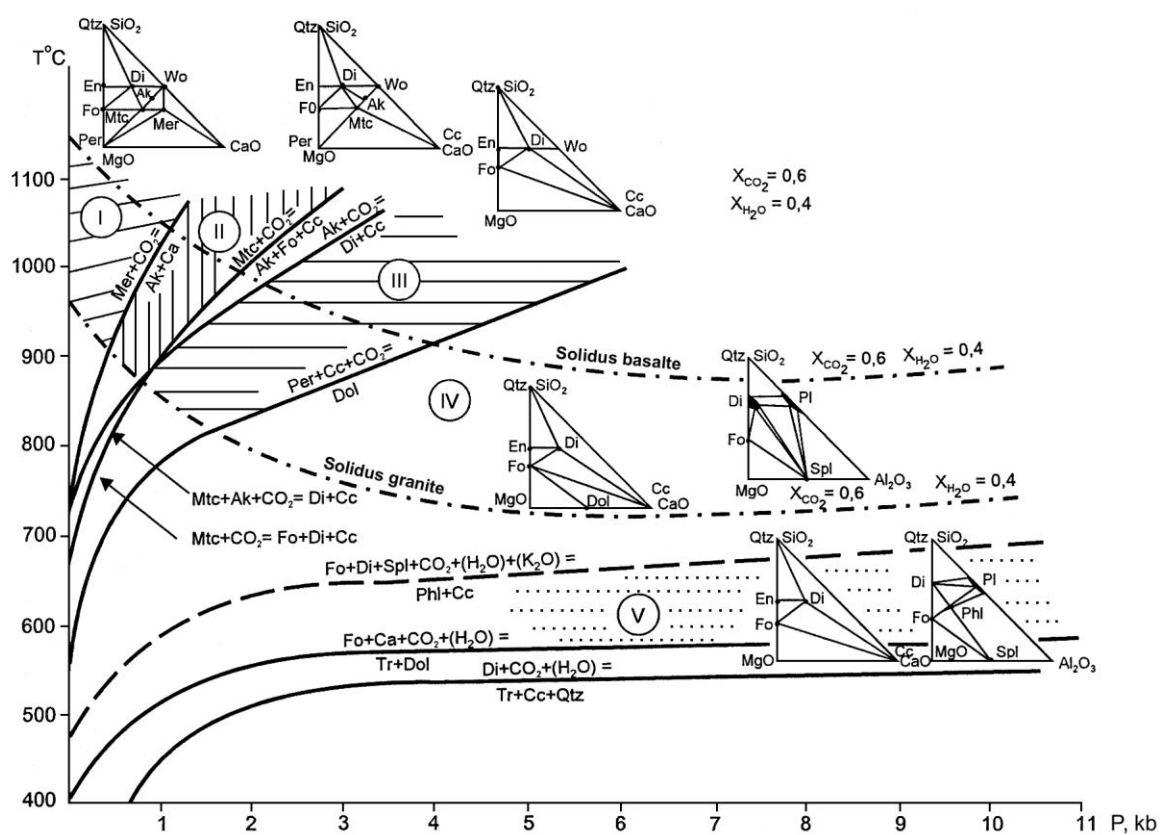


Fig. 16.6. Diagram of dependence of parageneses of magnesian skarns upon T-P at $X_{\text{CO}_2} = 0,6$, $X_{\text{H}_2\text{O}} = 0,4$.

Calculated on experimental data. I-IV – facies of depth of magnesian skarns; V – parageneses of magnesian skarns at postmagmatic stage. basalt solidus; granite solidus

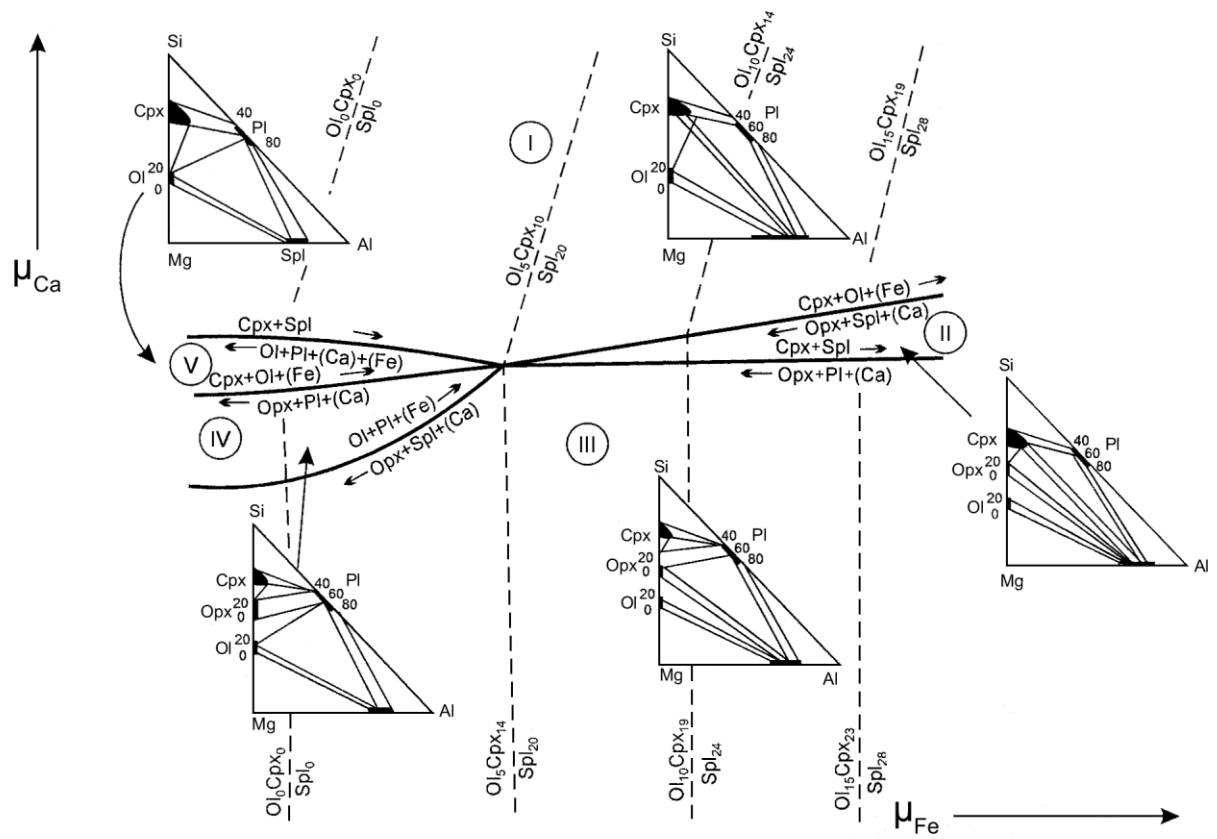


Fig. 16.7. Diagram of dependence of parageneses of magnesian skarns at magmatic stage upon chemical potentials of calcium and iron.

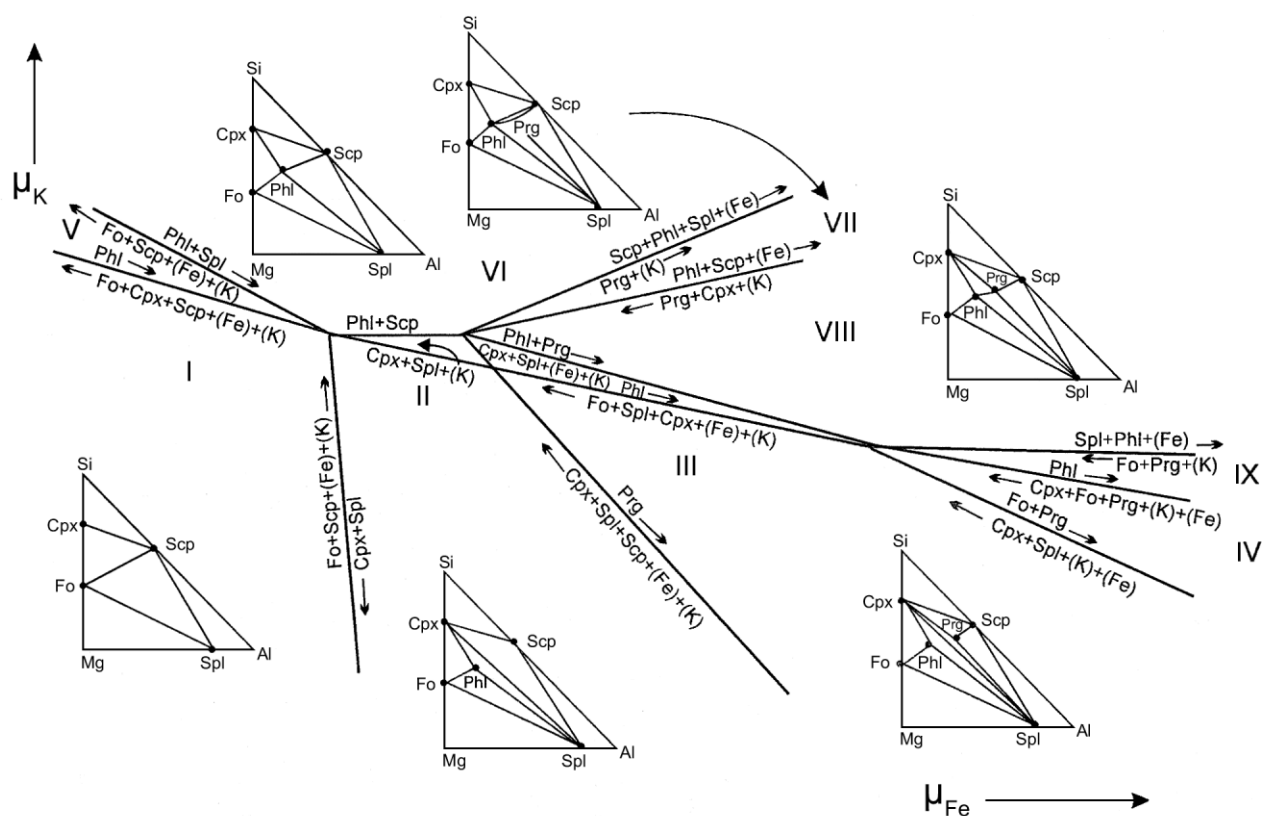


Fig. 16.8. Diagram of dependence of parageneses of magnesian skarns at magmatic stage upon chemical potentials of potassium and iron.

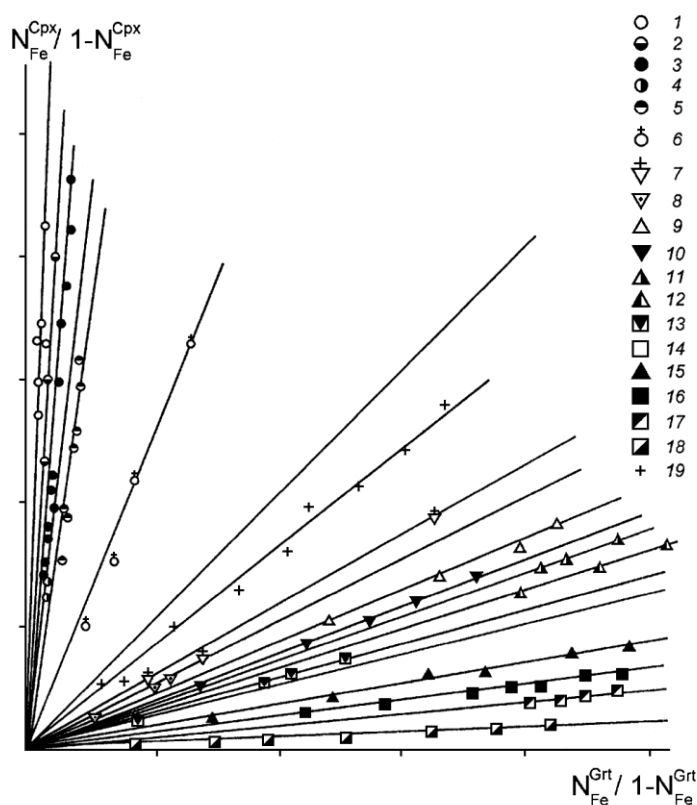


Fig. 16.9. Diagram of coexisting compositions of pyroxene and garnet for different deposits in calcic skarns.

1-tungsten deposit of Ingichka, Uzbekistan; 2-tungsten deposit of Fuyogatin, Japan [Yto, 1962]; 3- tungsten-polymetallic with SnO_2 deposit of Maikhura, Tadjikistan; 4 - tungsten-polymetallic with SnO_2 deposit Lost River, Alaska [Dobson, 1982]; 5 – molybden-tungsten deposit of Tyrniauz, Russia; 6 – tungsten deposit with polymetals and gold, British Columbia, Canada [Ettlinger and Roy, 1983]; 7 – copper deposits with gold, British Columbia, Canada [Ettlinger and Roy, 1983]; 8 – copper with tungsten deposit of Darinskoe, Russia [Indukaev, 1980]; 9 – polymetallic deposit, Empire, New Mexico [Burton and al, 1982]; 10 – Turin copper deposit [Podlesski, 1979]; 11 - polymetallic deposit, Kansai, Tadjikistan; 12 - polymetallic deposit Tamperico, Italy [Burton et al., 1982]; 13 – copper – iron – deposit of Milko-Tirnov, Bulgaria [Vassiliev et al., 1964]; 14 - Gorno-Blagodatskoe and Vysokogorskoe iron deposit , Russia [Podlessky, 1979]; 15 - polymetallic deposit Altyn-Topkan, Tadjikistan; 16 – iron – ore deposit of Gorna Shoria, Russia; 17 – iron –ore with ilvaite and sphalerite deposit of Kern, New Mexico [Burton et al., 1982]; 18 – iron – ore deposit of distinct of Fudjay, China [Zhao – Yiming et al., 1982]; 19 – other skarns manifestations.

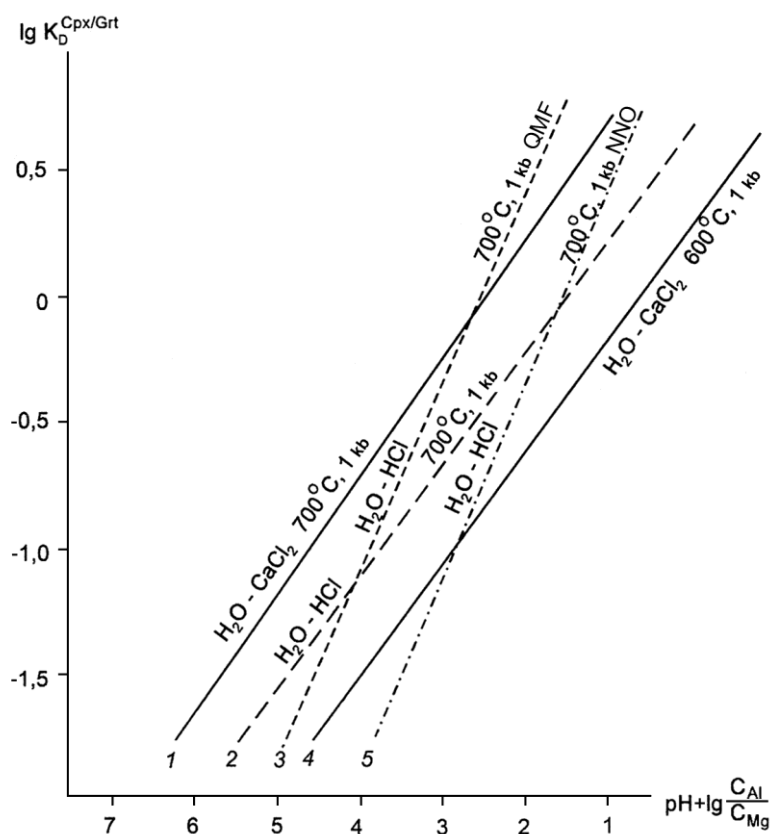


Fig. 16.10. Dependence of logarithm of distribution constants of iron between pyroxene and garnet ($K_D = \frac{X_{Fe}^{Cpx}}{1 - X_{Fe}^{Cpx}} \div \frac{X_{Fe}^{Grt}}{1 - X_{Fe}^{Grt}}$) upon acidity of solutions ($pH + \lg C_{Al}/C_{Mg}$) on experimental data [Zharikov & *al.*, 1979].

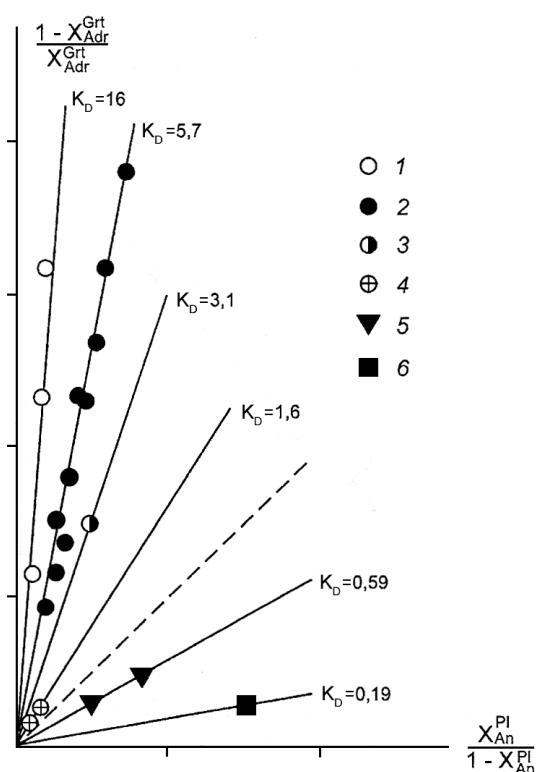


Fig. 16.11. Coexisting compositions of garnets and plagioclases in different skarn deposits.

1 – tungsten deposit of Ingichka, Uzbekistan; 2 – tungsten sulfides deposit of Maïkhura, Tadjikistan; 3 – molybden – tungsten deposit of Tyrnauz, Russia; 4 – molybden – tungsten deposit of Chojruh-Dajron, Tadjikistan; 5 – Turin copper deposit, Russia [Podlessky, 1979]; 6 – Tyshelginskoe, Russia [Miroshnikov & *al.*, 1969]

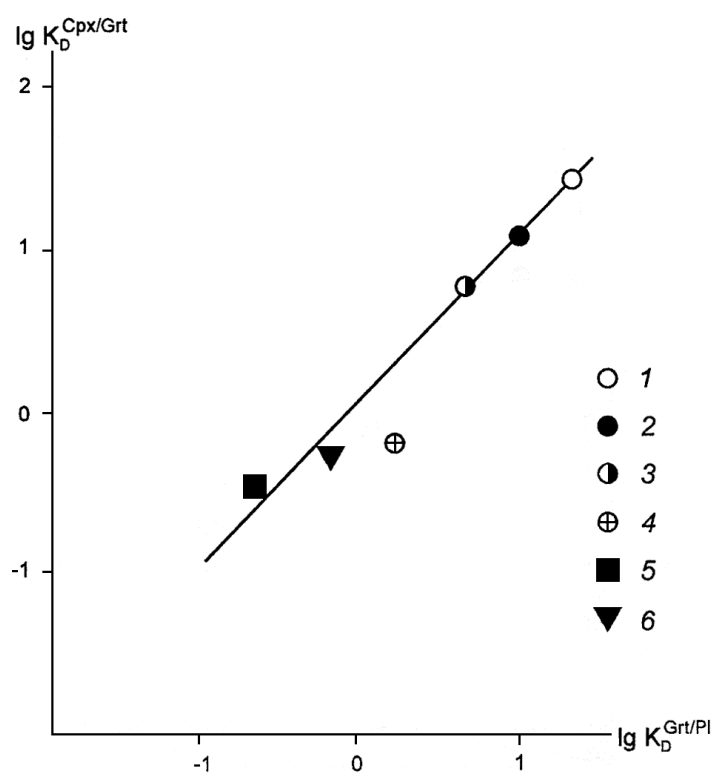


Fig. 16.12. Comparison of distribution constants distribution of $K_{\text{Fe}}^{\text{Cpx/Grt}}$ et $K_{\text{Al}}^{\text{Grt/Pl}}$ as indicator of acidity for various skarn deposits.
 Symbols as in fig. 16.9 and 16.11.

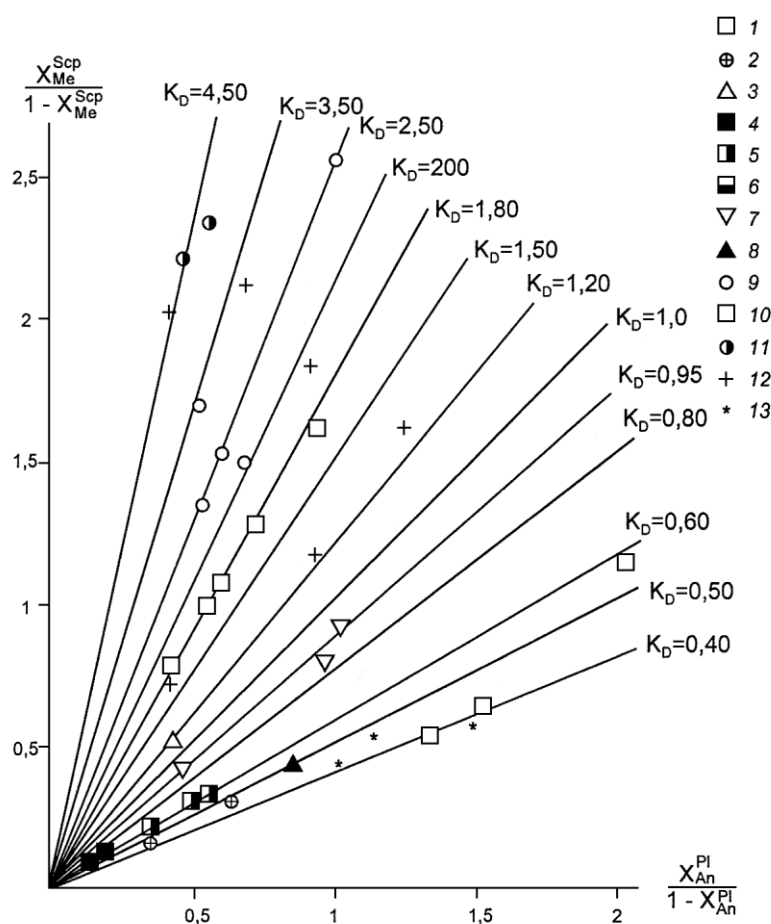


Fig. 16.13. Coexisting composition of scapolite and plagioclase

1 – skarn deposit of Gavasay, Uzbekistan ; 2 – skarn deposit of Choirux-Dairon, Tadjikistan ; 3 – skarn deposit of Ak- Djilga, Kirghistan; 4 – skarn deposit of Lebazhin, Russia ; 5 – skarn deposit of Sokolovo – Sarbay , Kazakhstan ; 6 - skarn deposit of Dashkesan, Azerbaidjan ; 7 – skarn deposit of Glafirine, Russia [Solodovnikova, 1964] ; 8 – phlogopite deposit of Emeldjak [Lazarev, 1963] ; 9 – skarn deposit of Aldan [Marakushev, 1958] ; 10 – skarn deposits of Quebec, Canada [Show, 1960 ; Haughton, 1975] ; 11 – skarns of Ontario province, Canada [Haughton, 1975] ; 12 – metamorphic shists and gneisses of Quebec and Ontario provinces, Canada [Haughton, 1975] ; 13 – other skarns manifestations at small depth [Show, 1960].

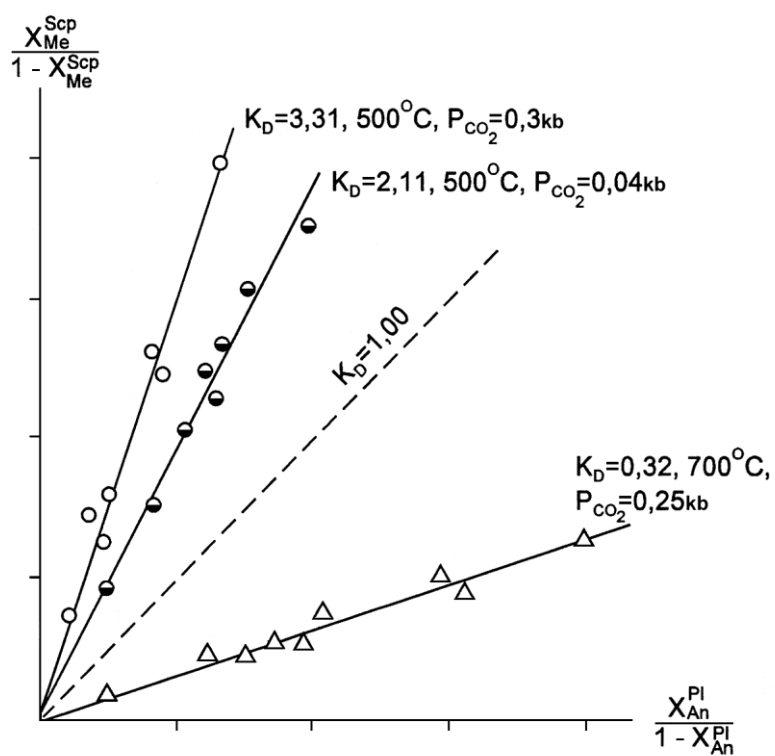


Fig. 16.14. Experimental determination of distribution constant of calcium minerals between scapolites and plagioclase [Kotelnikov, 1977].

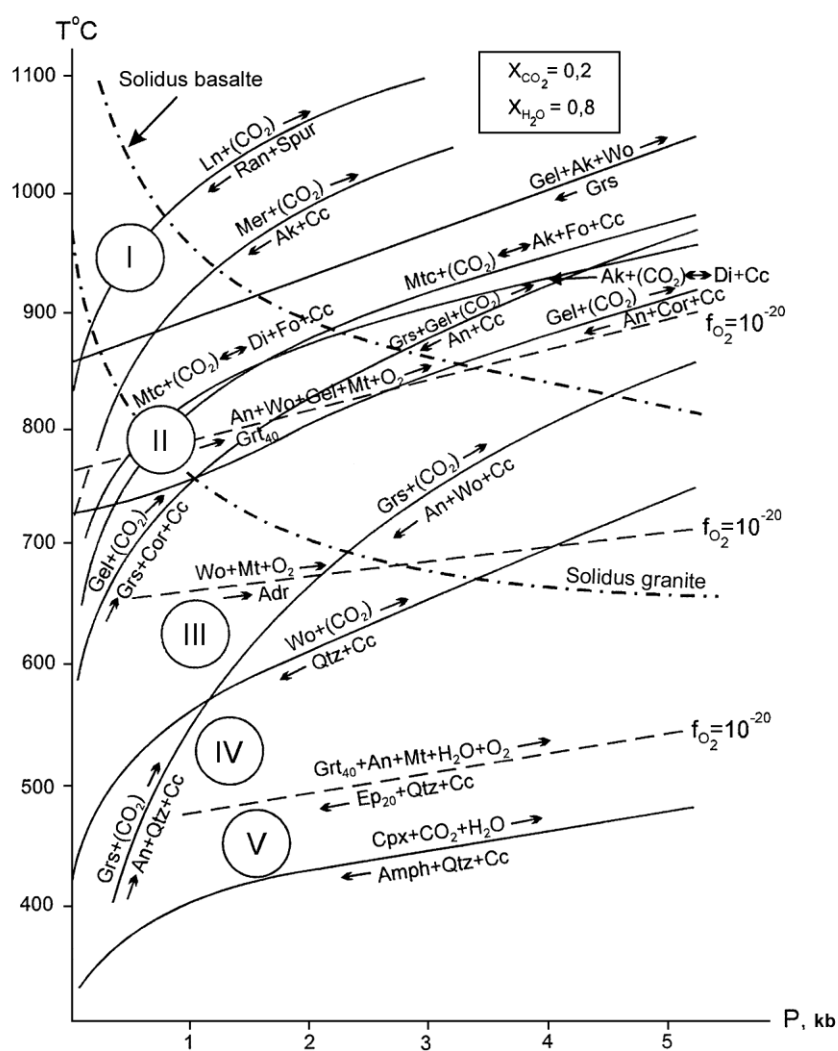


Fig. 16.15. Main border minerals in equilibrium of calcic skarns calculated for condition of $X_{H_2O} = 0,8$, $X_{CO_2} = 0,2$ from experimental and calculated data.

Equations of reaction are described in univariant lines. For reaction with Mt et O₂, oxygen fugacity is taken as $f_{O_2} = 10^{-20}$. Position of granite and basalt solidus melts calculated for $X_{H_2O} = 0,8$, $X_{CO_2} = 0,2$.

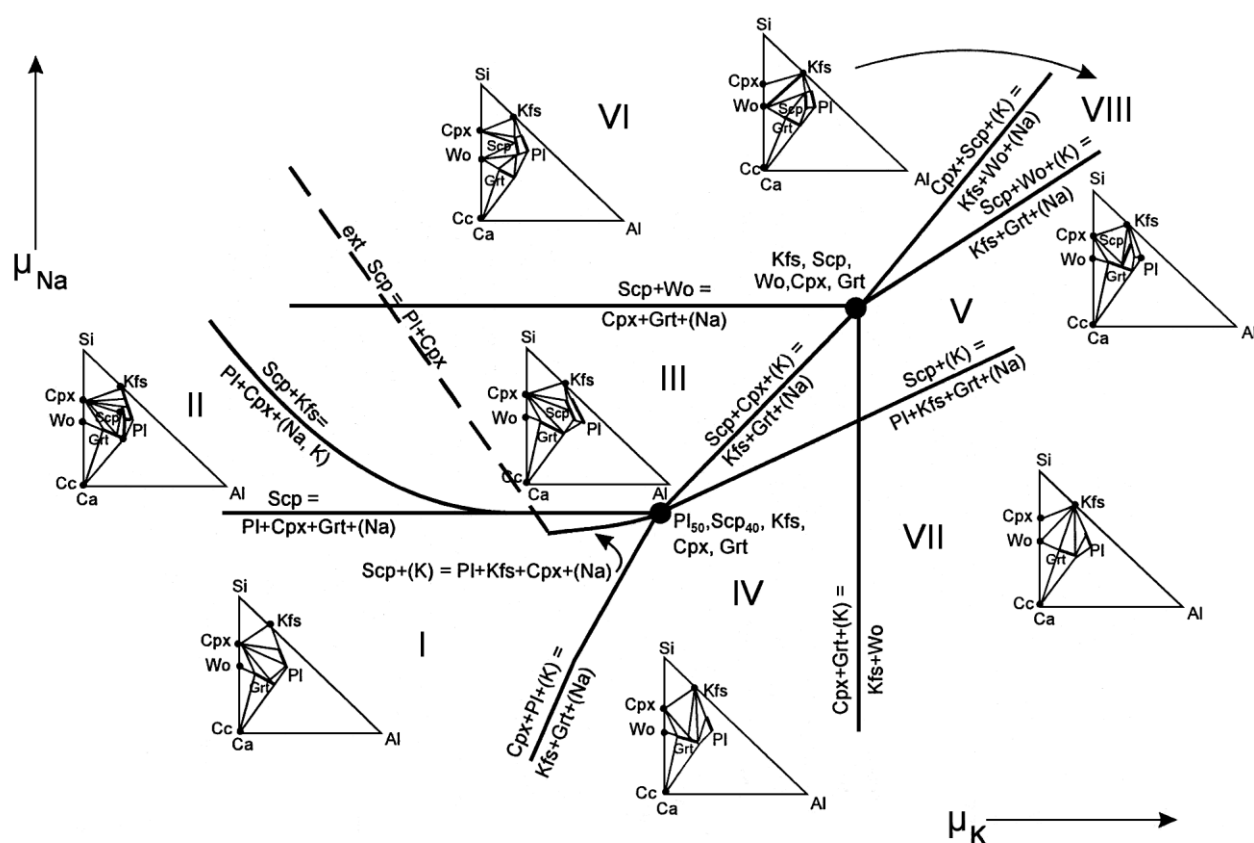


Fig. 16.16. Diagram of dependence of parageneses of calc skarns upon chemical potentials of potassium and sodium.

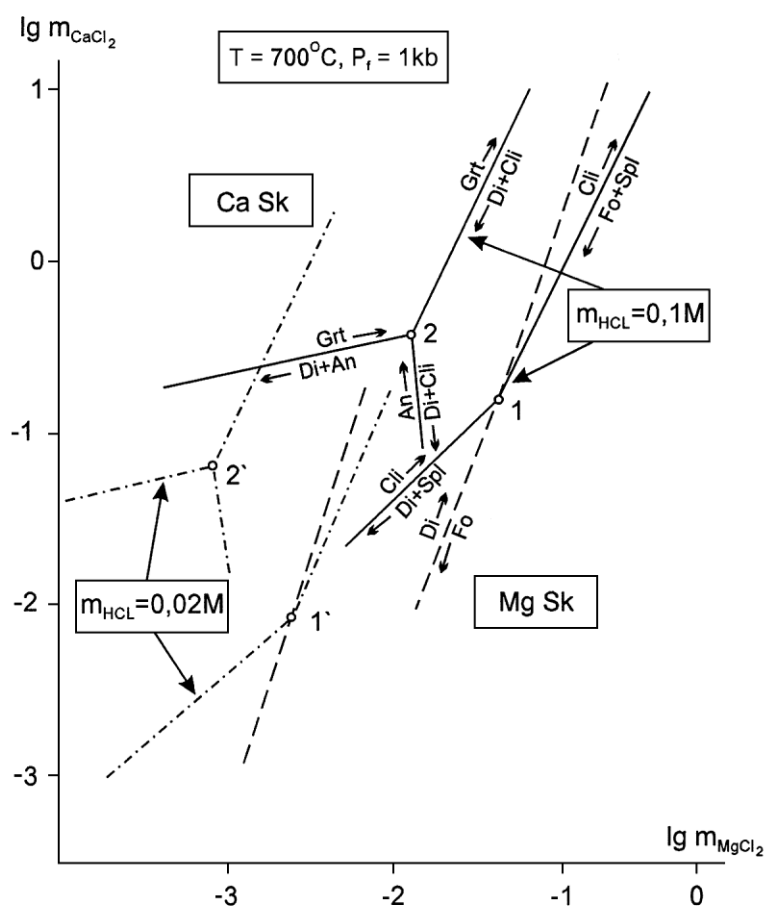


Fig. 16.17. Diagram of dependence of parageneses of calcic and magnesian skarns upon CaCl_2 , MgCl_2 and HCl .

Results of experimental researches at $T = 700^\circ\text{C}$ and $P = 1 \text{ kbar}$ [Zharikov & Khodorevskaya, 1987]. Unbroken and dashed lines, experimental results at $m_{\text{HCl}} = 0.1 \text{ M}$ and $m_{\text{HCl}} = 0.02 \text{ M}$. Dotted line, calculated data.

CHAPTER 17

Greisens

Definition. Greisens are high or middle temperature metasomatic rocks of quartz-mica, quartz-topaze or quartz-tourmaline composition accompanied by deposits of tin, wolfram, molybdenum, beryl and genetically akin to leucogranites. The link of greisens with rare metals Sn-W-Mo-Be mineralizations is obvious and in the Russian literature the term «greisen deposits», introduced by V.I.Smirnov, has been generally admitted.. In western literature a similar notion is absent, and the deposits are designated by an important metal name (W, Mo, Sn, Be deposits). Originally the term greisen designated essentially quartz-muscovite rocks, formed through metasomatism of rocks of granitic composition, sandstones, schists and volcanogenic rocks. The process of greisen formation is consequently called greisenization. Subsequently to the term «greisen» was attached a formation significance and under this designation was understood an aggregate of metasomatites, formed by greisenization. So the narrow significance of this term is preserved, designating a rock of a determined mineral composition. Slightly or moderately transformed varieties are usually called greisenized rocks.

Amongst constant evidence of greisens are found 1) a tight spatial and genetical link with ultra-acid granites ; 2) a specific collection of rare metals (W, Mo, Sn, Be, Bi) ; 3) characteristic types of periorite alterations, i.e. greisenization, reflected by the development of quartz, white micas, topaz, fluorite, tourmaline ; 4) high participation in the processes of mineral formation of volatile acid components : F, Cl, B, S, CO₂ [Nakovnik, 1954 ; Shcherba, 1968, Rundqvist *et al.*, 1971]

Geological setting and correspondances with other metasomatites.

The main geological and-structural features accompanying greisenization are [Rundqvist *et al.*, 1971]: 1) fringe zones of intermediate massifs of folded domains; 2) external fringe zones of folded domains; 3) zones of uplifted internal anticlines of folded domains; 4) zones of internal activation of domains of completion folding. Granites with which greisens are related, are of

postorogenic type. These enter regions of stability, developing diapirs having at their basis a mantle plume and zones of lesser density in the upper mantle and lower crust. The interval between completion of the geo-synclinal regime and intrusion of postorogenic granites reaches 75-100 million years .

Greisenized rocks spread in near-contact zone and in the roof of granitoid intrusions, mainly in those of higher silicic acid composition. Most greisen deposits are confined to bodies of granites, small compared with the surface showings, but the greisens of exocontacts are partially related to dike belts.

The morphology of parts of greisenization in endocontacts, is basically determined by the shape of intrusive contact, but in enclosing rocks the greisens are localized in zones of tectonic dislocation.

In most cases, a direct genetic link is not indicated with defined discrete small granitic intrusions. It is most probable [Omelyanenko, 1978] that greisenized solutions have a deeper source, and their link with concrete granitic bodies is paragenetic. The basic lines of the geological position of greisens is well illustrated, for instance, by the wolfram-molybdenum greisen deposit of Akchatau in Kazakhstan [Zharikov & Zarskiy, 1995]. This deposit is localized in cupola parts of a granitic pluton (fig 17.1 and 17.2). According to gravimetric data the massif has the shape of a lopolith, extending in length on 28 km, in breadth to 12-16 km and in thickness to 7-8 km in the central part. The greatest part of the granite body is deeply hidden in terrigenous deposits of upper Silurian and in acid and intermediated effusive Carboniferous rocks. The diameter of the outcropping cupola is nearly 4 Km. It is supposed that the Akchatau pluton is mainly composed of coarse grained porphyroid granites at first phase of penetration (cf. fig 17.2). Flat bodies of medium-grained granites at phase II are concentrated towards cupolas and apical crests of the massif. Fine-grained granites of phase III form small rods, dikes and more complex bodies of stepped type in granites of phases I and II [Shcherba, 1960]. In chemical and mineral composition the granites of the three phases are similar, and are related to subalkaline leucocratic granites with predominance of potassium and sodium. Country rocks around the Akchatau are hornfelsed in the distance of 800 to 1000 m.

About 300 small vein-greisen bodies in general quantities are spread on all the outcrop of the granite cupola, but predominantly at their periphery. All the small bodies are confined to the upper near-contact part of the massif and extend with a thickness not exceeding depth to 40-60 m, but extending to tens and hundred of meters with a 3m thickness. Their industrial value is of low importance. The basic supply of W-Mo ore at Akchatau are concentrated in a few coarse veinous bodies at the S-E slope of the cupola. These bodies are controlled by elongated fractures which have a submeridional direction and steep dip. Ore veins are characterised by thickness increase in the direction of the contact surfaces of granite massif with dissociation of one greisen body in a serie of

subparallel and fan-like smaller upwards flowing greisen bodies (“greisen bundels”) [Bogoplov *et al.*,1971]. The extension of such bodies reaches in length 2-3 Km, in breadth 500m with a thickness 2-3 to 20-50m. Wolframite and molybdenite form thin dissemination and also nests and veins, in association with quartz, phlogopite, beryl, muscovite, topaz, pyrite and dickite. Industrial mineralization is concentrated in compact quartzic greisens and quartz veins, in which are localized the richest ores ; rich global reserves are nevertheless situated in the greisens [Shirkunov, 1981]. Quartz veins, as a rule, occupy an axial position in greisen bodies, but some appear later in age.

Thick greisen bodies in granites are modified in the roof zone in series of thin veins, with formation of linear and net-like stockwork with a productivity that rapidly falls with distance from contact [Gulyaeva ,1978]. On the whole, in Akshatau, endocontact bodies within granites rarely predominate , and the rocks of the roof are weakly greisenized.

Greisenization in Akshatau and other deposits is accompanied by other metasomatic transformed rocks, for instance, albitization and potassic-feldspathization of granites, skarnization, propylitization-albitization and potassic-feldspathization precede greisenization and occupies wider near-contact domains in granitic massifs. On the other hand greisenization may extend far away from the contact by violent fracturation of the roof. Greisens affix themselves on skarns at the contact of granites with carbonatic rocks. Propylitization at postmagmatic stage arises later after greisenization at lower temperature and occupies a greater volume of rock either in exocontacts-or endocontacts of the granites. A schematic sequence of processes including greisenization is indicated on fig.17.3.

Facies of greisens and metasomatic zoning. In the mineral composition of internal zones of metasomatic zoning in greisens, a few facies are distinguished depending upon the greisenization solution and the replaced rocks. According to these last criterion, greisens are distinguished into aluminosilicate rocks (granites, quartzo-micaceous schists, sandstones) and rocks poor in silica and alumina (carbonates and basic magmatics). In the first group are distinguished the following facies : quartz-muscovite, quartz, muscovite, muscovite-feldspar, quartz-tourmaline, quartz-topaze. In the second group are distinguished only two non- quartzic facies : phlogopite-muscovite and feldspar-fluorite.

A typical column of metasomatic zoning in apogranitic greisens has the following aspects : 0) unaltered granite (quartz, calcic feldspar, oligoclase, biotite, magnetite) ; 1) muscovitized granite (quartz, calcic feldspar, albite, muscovite, biotite, magnetite) ; 2-3) greisenized granite 2) quartz, calcic feldspar, albite, muscovite ; 3) quartz, calcic feldspar, muscovite) ; 4-6 (greisen (4-quartz, muscovite ; 5-quartz, topaze, 6- quartz). Topaze and monoquartzic zones are frequently absent. For exotic products of greisenized limestones

zoning is different : 0) limestones ; 1) calcite, fluorite ; 2) fluorite, muscovite ; 3) fluorite. However, in the products of limestone greisenization are present albite and phlogopite.

The greisen bodies of Akshatau cover a well expressed lateral and vertical metasomatic zoning [Bogopelov *et al.*,1971]. In axial parts of all big ore bodies, traditionally named at Akshatau « ore veins », is established a monotypic replacement by compact quartz veins, passing vertically upwards to porous quartz greisens, then to quartz-topaze and quartz-muscovite greisen (fig 17.4). In the limits of greisen bodies basic industrial ores occupy a determined hypsometric level, delimited by a zone of development of compact quartz greisen and by the lower part of quartz-topaze greisen, but above and beneath mineralization is weaker. In a longitudinal projection of this so-called « ore belt » [Tchukrov, 1960], it has the aspect of a near-horizontal ore lens. Vertically it totals 150-200m, and moreover, in axial quartz veins, industrial mineralization extends to 20-50m, higher than in the greisens surrounding them [Bogopelov, 1992].

Lateral metasomatic zoning in all basic ore-producing horizons within the « ore belt » has an unique structure (fig. 17.4b). The body's central part immediately contiguous to the axial quartz vein is composed of a mineralized compact quartz greisen, replaced in both directions by ore-free quartz-topaz greisen and quartz-muscovite greisen, greisenized granite replacing leucocratic granite. In the upper, supra-ore part of the greisen body (cf. fig 17.4.A) an internal zone of quartz greisen is lacking and the lateral zoning has the following structure :

Quartz vein 0	Qtz-Toz greisen 0.55	Qtz-Ms greisen 1.0	Greisenized granite >14m	Leucocratic granite
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In the lower sub-ore horizons (cf. fig. 17.4, C), the quartz-topaz zone of the greisen falls, but the thickness of the other zones, particularly the quartz greisen zone, increases [Gotman & Malakhova, 1965].

Quartz vein O	porous quartz greisen 9.5	Quartz muscovite greisen 10,5	Greisenized granite > 14 m.	Leucocratic granite
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Total thickness of strictly greisen zones (without greisenized granites) usually varies from 10-20cm to 1-2m. Relatively weak lateral zoning, apparently due to diffusion. Vertical and longitudinal zoning of big greisen bodies, is measured in tens and hundreds of meters, undoubtedly linked with infiltration.

Chemistry of greisenizing process. In greisenization two extreme cases are observed: 1) process with accumulation of silica ; 2) process with accumulation of alumina.

In the first case, the quartz content increases in the rocks, for instance, from 30-35 volume % in granite to 70-90 % in quartz-topaz or to 60-80 % in muscovite-quartz greisens. To this are related removal of alkali, alumina, but also calcium, magnesium and iron. Alumina accumulation leads mainly to the formation of muscovite or of topaz greisens. In these cases, quartz content in rocks approximates 9-10%, but muscovite and topaz content reaches 70-90%. Apparently, alumina accumulation may promote as decrease in acidity of greisenized solutions.

Calculated addition or subtraction of rock-forming components for the Akshatau deposit, based on data of grid-sampling [Gotman & Malakhova, 1965 ; Zraisky *et al.*, 1994] show that granitic greisenization induces steady subtraction, from all zones, of Na_2O and K_2O , addition of SiO_2 , Fe, F, H_2O , CO_2 and rare metals. Alumina is subtracted in great amounts from the lower parts of the greisenized body and redeposits in the upper parts, at the level of development of quartz-topaz and quartz-muscovite greisens in axial zones of big greisen bodies (17.5)

Physico-chemical conditions of mineral formation. Physico-chemical conditions of greisenization were studied in detail and are exposed below in the example of the Akshatau deposit. They rather well characterize the typical greisenization processes [Zraisky *et al.*, 1994].

Temperature evolution. On data of two-feldspar and oxygen-isotope geothermometry, T of crystallization of I, II and III phases of leucogranite intrusions amounts to 750, 700 & 650 °C (± 50 °C) Formation of chambered pegmatite arises between 620 and 560 °C (± 40 °C). Comparison of results on oxygen isotope distribution in mineral greisens and ore veins of Akshatau [Korotaev *et al.*, 1988 ; Zharikov *et al.*, 1982] with data on fluid inclusions [Doroshenko & Pavlun, 1981 ; Korotaev & Matveeva, 1989 ; Reif, 1990] permits rather definitely to say that the formation of greisens and the localization of W-Mo mineralization, on the whole, occupies the high temperature interval between 550 and 350 °C. Quartz veins are formed, on average, at 60°C lesser than the greisens they contain. Temperature of 350°C, apparently, indicates the lower limit of the Akshatau proper greisen-ore stage by deposition of the principal mass of rare metals (W, Mo, Be, Bi, Sn) Lower temperatures (350-150°C) are related to terminal sulfide stages of ore processes in the course of which may arise also some recrystallization of earlier W-Mo ores [Bogopelov, 1979, 1992]. On the basis of mineral paragenesis of contact hornfelses it is possible to suppose that their formation in a thermal field of granite massif arises at temperatures from 450 to 350 °C.

Pressure evolution. On paleolithological reconstructions, structural and morphological properties of granites, the thickness of rocks of the roof at the time of formation of the Akshatau pluton is evaluated by various authors from 1 to 4 km, which correspond to a lithostatic pressure of 0.3 to 1.0 kbar [Shcherba, 1960 ; Rare metal mineralization, 1988 ; Nergei, 1983]. On calculated data of F.G. Reif, [1990] founded on P-V-T correlations in melt inclusions in the quartz of the granites, the fluid pressure in deep residual focus at the beginning of phase III intrusion attained 4.2 to 4.8 Kbar. However, a systematic study of fluid inclusions in veins of mineral ore bodies of Akshatau [Doroshenko & Pavlun, 1981 ; Pavlun, 1984 ; Korotaev *et al*, 1994] indicates that the fluid pressure in the course of the main ore stages periodically varied from 1.6 to 0.5 Kbar, and at later stages decreased to 0.2 Kbar. At the same time [Korotaev, 1994] is also displayed a group of high density inclusions with P from 0.8 to 2.8 Kbar, homogenized in the liquid phase in the narrow temperature interval of 350-400 °C.

All the determined data, possibly do not contradict one another but reflect a complex evolution of the fluid-magmatic system. If we take that the Akshatau intrusion was formed at depth of about 3 Km, fluid pressure in its upper part could approximate the lithostatic pressure and reach about 1 kbar. In the deep part of the intrusion pressure attained 2-3 Kbar and could rise even higher at retrograde boiling of the magma, and thus oscillate as a result of the system decompression.

Fluid regime of mineral system. On data of F.G. Reif [1990] the initial water content in melt phase I of the Akshatau granite massif increased and attained 4.5 ± 0.5 weight %. It increased even more due to the crystallization differentiation of the magma and attained 5.2 ± 1.2 weight % in phase II and 6.7 ± 1.5 in phase III. Salinity of this magmatogene fluid was insignificant. On data of cryometry of peculiar fluid inclusions, it is limited to 13-23% eq. NaCl. It is supposed that the chief saline components are Na and K chlorides and fluorides, but admixture of Mg, Fe, Ca, Li chlorides all in all does not exceed 1 %. The basic fluid consists of water containing CO₂ and insignificant quantities of other gases. Apparently in magmatic fluid, chlorine predominates on fluorine, although the role of fluorides was also important, as evidenced by tentative evaluations of HF concentration (0.2-0.8 m) in rock-forming biotites [Zaraisky *et al.*, 1994]. Due to granite crystallization, HF content in the residual melt has increased. At the same time the activity of melt and of the aqueous fluid in equilibrium with the melt increase and determine the evolution of the Si/Al and (Mg + Fe)/Al ratios in biotites from phase I to phase III. On the basis of Fe and Mg distribution between biotites and super critical chlorid fluids, it is possible to conclude that the Akshatau magmatogene fluid was characterized by a high Fe/(Fe + Mg) ratio extending from 0.85 at crystallization of phase I to 0.90 at crystallization of phases II and III. We may also confidently speak of an

increasing Mn activity in the melt and in the fluid in equilibrium on the basis of its noticeable content in biotite (up to 2.6 weight % MnO) and especially in ilmenite (up to 24 %).

In magnetite, ilmenite and titanomagnetite of all phases of leucogranites, W often occurs in quantities sufficient for microprobe determination (up to 0.1-0.2 weight % WO₃ in phase I and 0.3-0.5 in phase III). Even higher WO₃ is measured in accessory ilmenorutile (1.3-1.4 weight %) and rutile (0.4-0.8 weight %) from dykes of microgranites.

Entry of wolfram into primary minerals of Akshatau granites and their enrichment in accessory minerals of later differentiates of magmatic chamber unravels its concentration in granitic residual melts and permits to suppose an orthomagmatic behaviour of the wolfram.

Postmagmatic solutions have a fluorid-chlorid-calcic-sodic composition and high saline concentration (table 7.1). Similarity of composition and concentration of magmatic and ore-forming hydrothermal fluids may serve as indicator of their genetic kinship and evolutionary inheritance. Laser-ablation analysis of fluid inclusions in quartz and fluorite from quartzic and quartz-topazic Akshatau greisens reveals high concentration of W (up to several g/l), of Mo (up to 0.7 g/l) and the presence of Cu, Zn, B and Ti [Basheev & al., 1986 ; Reif, 1990]

Table17.1. Succession and physico-chemical parameters of mineral formation in ore bodies of Akchatau deposit after data of study of fluid inclusion [Doroshenko & Pavlun, 1981 ; Pavlun, 1984 ; Pavlun & Simkiv, 1982]

Mineral association	T°, C	P, bars	Fluid composition	%mass concentration, eq. NaCl+KCl
Molybdenite-quartz	440–320	1200–1000	Chloridic-hydrosilicato-sodic	41–27
Rare-metals, molybdenite-wolframite-quartz	480–300	1600–700	Fluoridic-chloridic-potassic-sodic	65–30
Pyrite-wolframite - quartz	415–260	750–500	The same	48–28
Galenite-sphalerite-	310–150	550–350	Hydrated carbonic-acid-	Not high

quartz			hydrocarbonic-sodic	
Phlogopite-quartz	180–80	~200	Substantially hydrated, potassic	Low
Zeolite-Quartz	60-20	~200	Idem	Low

Analysis of regular minerals formed at magmatic and postmagmatic stages of evolution of the ore-magmatic Akshatau system leads to the conclusion that the occurrence of acid greisenized fluids enriched in F, Cl, B and other volatile acid components do not arise at the earliest, but at sufficiently advanced stages of crystallization of the granite melt. This was already observed by G.N. Shcherba [1960], who stressed the special role of the coarse-grained granites of phase II, after emplacement of which in Akshatau began an active hydrothermal regime. F.G. Reif has established that there is lacking of independent fluid inclusions in quartz of phases I and II, and first appears together with melt inclusions in veins of derivatives of phase II and especially in products of phase III [Reif, 1990]. Replacement of the main products of the rare-metal stage of ore deposition (W, Mo, Be, Bi) by much later sulfide-quartz (Cu, Zn, Pb Bi) is accompanied by replacement of highly concentrated fluorido-chloridic solutions by more diluted chlorido-hydrocarbonatic ones, carbon dioxide enriched (cf. table 17.1) [Doroshenko & Pavlun, 1981]. Fluid pressure then falls to 550-380 bar, temperature decreases to 310-150 °C.

Greisens and metallization. Greisens are related to industrial concentrations of tin, wolfram, molybdene, beryllium, lithium and bismuth. Mineralizations of tantalum, niobium, zirconium and rare earth elements, formed in greisenized rocks, are linked with earlier processes of albitization. Formation of minerals occurs at various stages of the process of formation of greisen-ore bodies and with a decrease of acidity and temperature of the process. The evolution of the greisen-ore process is exemplified by Akshatau for which have been proposed models of evolution of a thermal field around and inside a cooling granite pluton. The results of modelling have permitted to evaluate the duration of the greisenization process and related ore-deposits (table 17.2)

Table 17.2. Life-span of evolution of the ore-magmatic Akchatau system (model of innermeasured differentiation of thickness of roof over granite cupola 1 km, introduction of II phase after 150000 years and initial temperature of granite melt 700° C)

Geological events and processes	Time, in 1000 years
Intruduction of phase I	0
Introduction of phase II	150
Introduction of phase III	180
Completion of crystallization of phase III	200
Formation of greisens: beginning end	200 300
Formation of quartz veins and: tungsten-molybdene mineralization beginning end	220 320
Completion of crystallization of phase II	320
Completion of crystallization of phase I	570
Sulphido-quartzic stage: beginning end	300 1000
Fluorite-quartzic and zeolite-quartzic stages	>1000

Thus, greisens are formed as a result of a hydrothermal high-temperature process of acid metasomatism with high activity of fluorine in the solution, and a strong link with post orogenic granitic magmatism. Greisenization follows albitization of granites, skarn formation, and precedes deposition of ore mineralization.

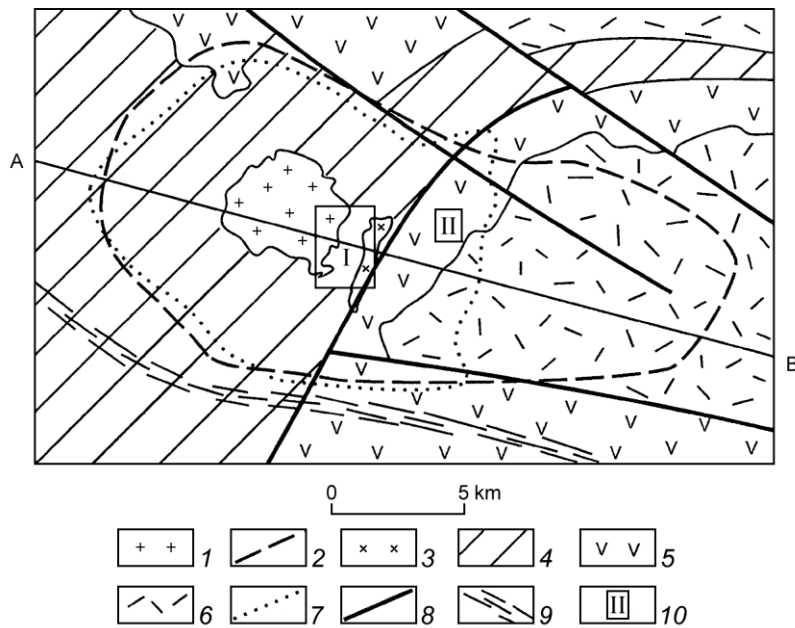


Fig. 17.1. Geological outline of Akchatau ore field.

1 – low Permian leucocratic granites of the Aktchatau complex (outlet cupola on surface); 2 – contour of the Akchatau intrusion at depth, on collective data of gravimetric survey ; 3 – adamellites C_{2-3} ; 4 – sandstones, schists, conglomerates S_2 ; 5 – lavas and tufas of andesites, dacites, liparites C_1 ; 6 – acid effusive C_{2-3} ; 7 – limit of contact aureole of hornfelses on surface ; 8 – tectonic break ; 9 – zone of deep fracture on geophysical data ; 10 – greisen deposits ;

I – Aktchatau, II – Aksay ; A – B line of geological cross-section.

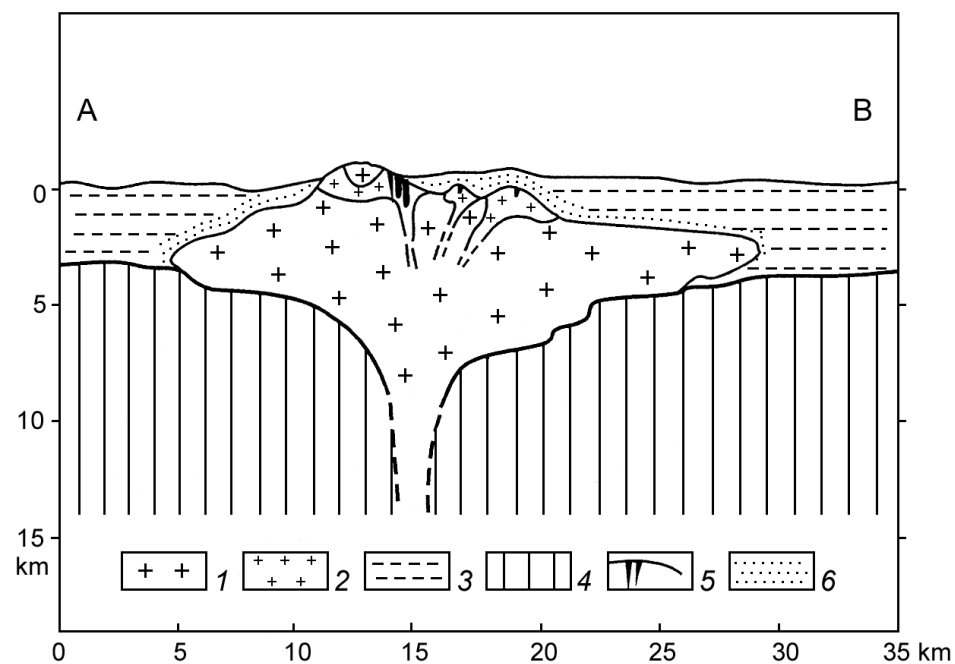


Fig. 17.2. Schematic longitudinal geological A-B cross-section (cf. fig. 17.1) of the Akchatau granite pluton, on collective geological, exploratory and geophysical data.

1 – coarse- grained granites of phase I ; 2 – middle- and fine-grained granites of phase II and III ; 3 – terrigenous and volcanogenous enclosing rocks ; 4 – crystalline rocks of precambrian basement ; 5 – ore bodies ; 6 – contact hornfelses.

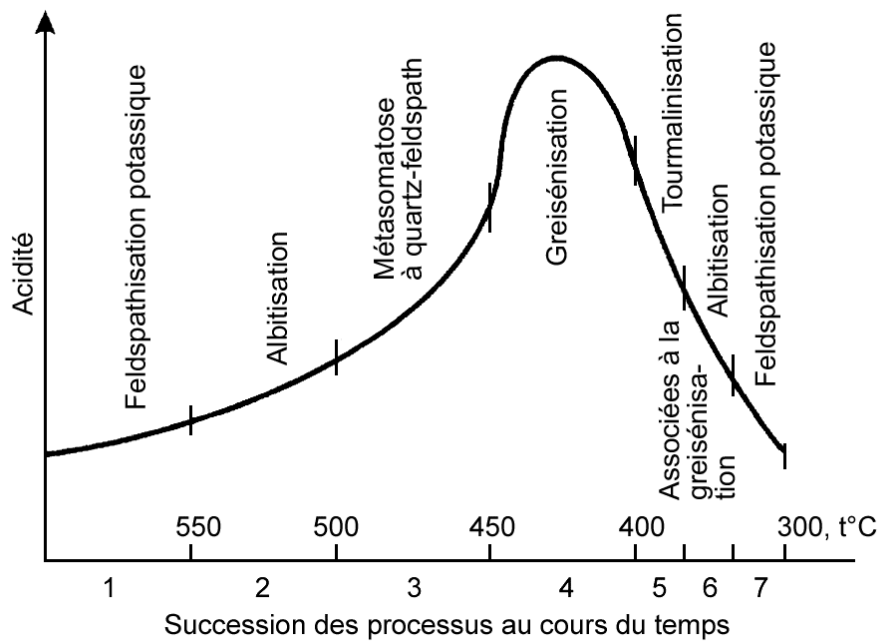


Fig. 17.3. Outline of evolution of acidity and temperature of postmagmatic solutions in time.

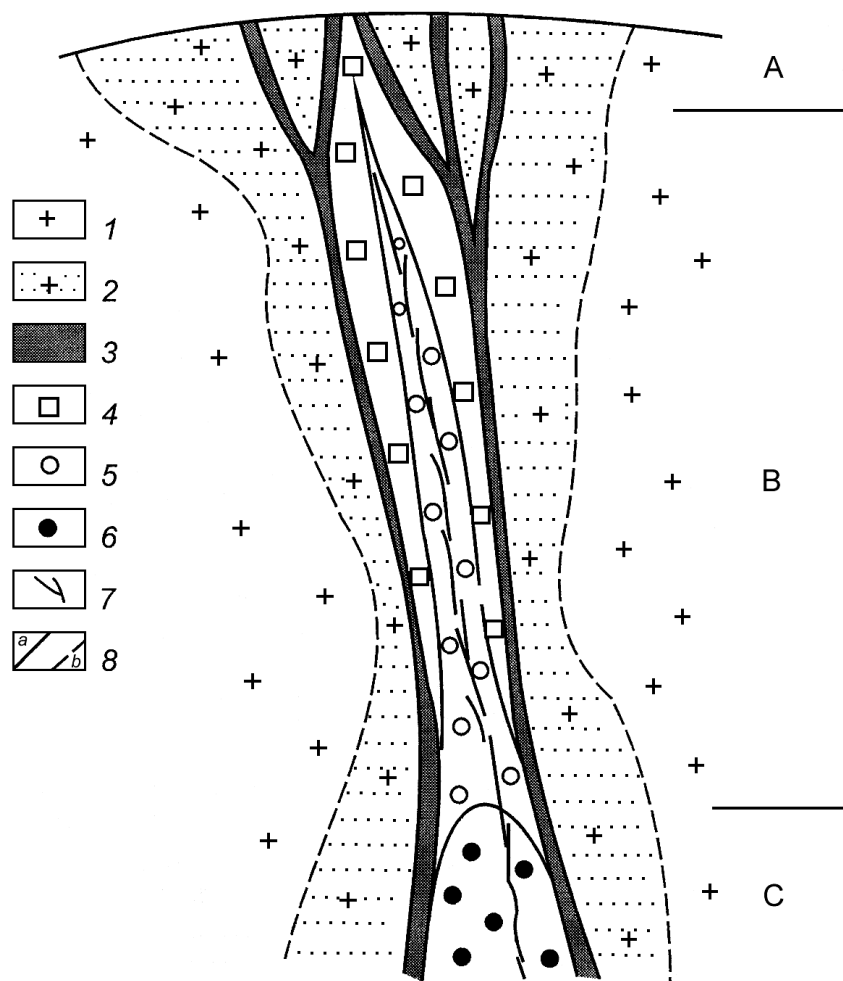


Fig. 17.4. Schematic lateral and vertical metasomatic zoning of main industrial greise bodies of Akchatau.

1 – medium- grained granites ; 2 – greisenized granites ; 3 – quartz-muscovite greisens ; 4 – quartz-topaz greisens ; 5 – dense quartz greisens ; 6 – porous quartz greisens ; 7 – quartz-ore veins ; 8 – limits of metasomatic zones (*a* – sharp, *b* - gradual) ; A, B, C – levels of greisen bodies with different types of lateral zoning.

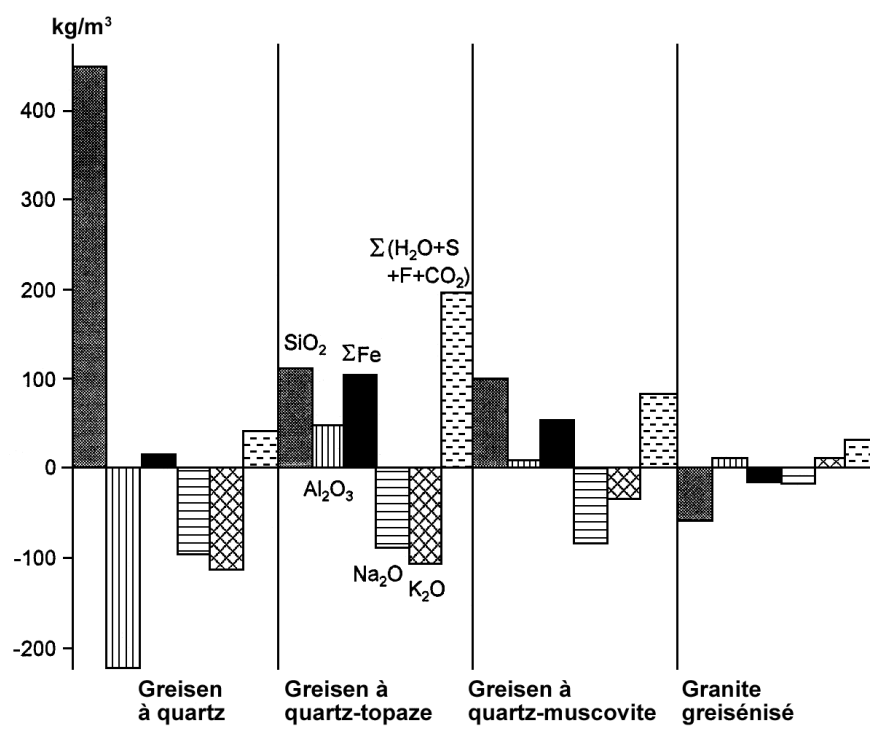


Fig. 17.5. Addition – removal of components at greisenization.

CHAPTER 18

Propylites and propylitized rocks

Definition. We call propylitized rocks greenstones who have suffered hydrothermal transformation. Unlike this wide notion, “propylites” have a quite definite petrographic significance: this is hydrothermal transformation of green andesites. Often, however, are called propylites generally any propylitization of rocks. Some authors choose a shorter term, and sometimes they mix up these notions and use the term propylite in different senses. To avoid confusion it is better to indicate which of them is meant.

Rock propylitization may form as a result of various processes 1) greenstone metasomatism of vulcanogene masses in regions of deposition of non-ferrous and noble metals (“propylites” in the terminology of F.Richthofen); 2) hydrothermal metasomatism of the argilization type in domains of active (and paleo-) volcanism, in which in deep zones of argilization together with clay-minerals are formed adular, albite, chlorite, in places also epidotes [Naboko,1963]; 3) a weak transformation of the rocks in the outer zones of periveinous acid metasomatism of the beretization and argillization type [Nakownik,1954]. Moreover, M.M.Vassilievsky[1970] identifies rock propylitization with products of regional metamorphism of greenschist facies based on affinity of mineral composition.

In all the enumerated types of processes, greenstone rocks are formed under the influence, principally, on magmatic rocks (but also on certain sedimentary) of feebly aggressive hydrothermal solutions from feebly acid to neutral at temperature in the range of 200-350°C. The narrow interval of variation of the external condition determines the generality of mineral composition and similarity of outer appearance of those greenstones formed in these processes. However, the peculiarities of geological position allows us to distinguish marked types of metasomatism from one another. In the first instance these distinctions are correlated with magmatism and ore deposition, which is clearly visible on the example of the various propylitized rocks and the

products of regional metamorphism. Propylitization is linked with intrusive hypabyssal and subvolcanic granitoids and their postmagmatic hydrotherms [Korzhinsky, 1948; Zharikov, 1959]. Within propylitized rocks are included zones of acid metasomatites and ore veins, but on the outer contour they border with unchanging (feebly changing) enclosing rocks. Unlike these, products of regional metamorphism, facies of green schist are included in regional metamorphic belts, no direct links are displayed with granitoid intrusions; regularly in them, ore depositions are formed in geological processes, not directly linked with immersion metamorphism. Rocks of greenschists facies border, on one side, with a prenite-pumpellyite or zeolitic, but on the other side, with an amphibolitic facies. Regional metamorphism arises with much lower CO₂ fugacity than the propylitization, under whose influence in metamorphism are stable prehnite and pumpellyite, uncharacteristic of propylitized rocks [Loginov & Rusinov, 1974; Rusinov, 1989].

During argilization of domains of active volcanism and outer zones of periveinous acid metasomatism are also formed rocks similar in mineral composition with the propylitized. However, they, forming an outer aureole around strictly argillites or berezites, do not prove characterized products of corresponding processes. They are only the result of the influence on the rocks of “exhausted” solutions losing their character. The main characteristic products of volcanic hydrotherm influence are facies of argillized rocks essentially consisting of clayed minerals, zeolites, opale, quartz and relict minerals. Such facies characteristic of the products of periveinous acid metasomatism may be quartz-sericite, quartz-kaolinite-alunite, quartz-sericite-carbonate etc. forming the inner zones of periveinous metasomatites.

Thus, the products of the enumerated processes, except the first one (Richthofen’s “propylites”) prove to be facies in the composition of an ensemble (formation) of argillized, berezitized and other rocks. Geologically independent formations are propylitized rocks in ore fields. They form the greatest volume of the rocks, usually comparable with the dimensions of the ore field, coinciding with small intrusions of porphyre granitoids formed in the process of their introduction, and after hardening they include ores of non-ferrous and noble metals and precede metal deposition. The ensemble, or formation of such propylitized rocks include a series of facies, distinguished in dependence upon composition of the initial rocks, temperature, oxygen fugacity and activity of calcium, sodium and magnesium. This complex of propylitized rocks, formed as an independent formation, presents the greatest interest for the study of a specific metasomatic process, propylitization and its products as hearths of enclosing mineralization. They receive therefore the main attention in the following exposition.

Propylitized rocks of various genetic types are composed of albites, chlorites, calcites and quartz. Usually they contain either pyrite or magnetite. In

medium temperature facies, moreover, there is typical epidote, actinolite and biotite. In near-surface high-gradient conditions at along with epidote, there may deposit prehnite and calcic zeolite (usually laumontite). They are quite often found in small quantities of sericite or hydromica replacing feldspars and chlorites. In feebly propylitized rocks olivine and orthorhombic pyroxenes are replaced by serpentine. In epithermal gold-silver deposits amid intensively propylitized rocks are present zones of adularization in which albite is mixed with calcic feldspar. D.Giusca [1965] has related adular-containing propylites to the “advanced phase” of propylitization. Apart from new mineral formations, in the composition of propylites occur also relict minerals of magmatic initial rocks, preserved owing to slowness of chemical reaction.

Geological setting. To the analysis of the geological position of propylitized rocks has been devoted an abundant literature [Korzhinsky, 1948, 1963; Nakovnik, 1954; Zharikov, 1959; Vassilievsky, 1970; Russinov, 1972, 1989]. The complication of the characteristic geological setting of propylitized rocks consists in the fact that, as remarked above, rocks with analogous mineral compositions are formed in various hydrothermal processes. Their varieties, occurring in the ore fields, starting with a progressive stage of hydrothermal magmatic process, i.e. at a time of advancement of a magmatic front, and isotherm surfaces, in the enclosing rocks were emitted in a genetically sole ensemble, or formation, of propylitized rocks [Rusinov, 1989] distinguished from other rocks of similar composition by the geological conditions of formations.

Formation of propylitized rocks begins parallel with magmatic replacement of enclosing series, but a zone of corneification of enclosing rocks separates this formation from the magmatic contact. . At a magmatic (progressive) stage resulting from the process of propylitization a vertical zoning is formed, in which a deep zone, close by a hornfels, is composed with biotite-actinolite, or biotite-epidotite, more rarely epidote- aktinolite or albite-calcite-chlorite facies. Moreover, a deep, high temperature zone is formed at the expense of the upper one. Biotitization spreads upwards along cracks in the form of steeply dipping linear zones in epidote-chlorite facies, moreover chlorite and albite of the upper zone are replaced by biotite and actinolite. An example of such interrelated facies of propylites in the gold ore deposits of Mnogovershinoe in the lower Amur Basin is shown on fig.18.1.

Propylites at the progressive stage characterize copper and molybdeno-porphyric, tin ore and epithermal gold and gold-silver deposits, linked with granitoid magmatism. Propylitization proves a pre-ore process and occupies a great volume of the rocks owing to encounter of meteoritic groundwaters reheated by fluids of magmatic origine. After crystallisation of the magmatic chamber and replacement of the progressive by a regressive regime in the ore fields a circulation continues of hydrothermal solutions whose temperature

decreases in time. Therefore isotherms change downwards and low temperature associations of hydrothermal minerals superimpose themselves on earlier, higher temperature ones. Then the associations, characteristic of propylites, may develop into skarns and hornfelses. Such propylitization at regressive stage, corresponding to that of increasing acidity in D.S.Korzhinsky's terminology, continues the propylitization of the progressive stage, but may also appear without it. As examples of products of "exclusively regressive" propylitization serve propylitized rocks in ore fields of pyrite deposits, facies of "feeble" change in the outer zones of periveinous zoning or deep zone of hydrothermal argilization in geothermal domains of active volcanism.

The geotectonic position of propylitized rocks is highly multiform. In risings of ocean bottom have been studied transformations of basalts, in which plagioclase is replaced by feldspar, pyroxenes by chlorite, smectite and calcite, but glass by smectites, chlorite and calcite. We also find high temperature association with epidotes and actinolite and albite. Investigations of their appearance in deep water drilling did not reveal, however, any characteristic of propylites of the zoning, such as propylitization of rocks of oceanic bottom occurring in very feeble vertical gradient of temperature. Formation on plagioclase of potash feldspar instead of albite may supposedly be linked with the influence of the composition of sea water on the temperature of plagioclase replacement by those or other feldspars [Rusinov, 1983]. In the form of appearance and geological setting, this aspect of metasomatism presents itself as specific process of transformation of basalts of oceanic bottom in rift zones and is not related to the formation of propylitized rocks in conformity to the data defined above.

In volcanic masses of initial geosynclinal depression spilitization processes appear widely similar in chemism to propylitization, but in geological setting and facies peculiarities relate to products of regional metamorphism. An approaching situation is observed in volcanic depressions of insular arcs, where are whole horizons of volcanogene sediments, chiefly pyroclastic rocks transformed into "green tufa". To the latter has been devoted an abundant literature concerned with Pacific insular arcs, in the first place Japanese and Kuril islands. These rocks compose stratified horizons of acid pyroclasts stretching on tens and hundreds of km. Magmatic minerals in them are replaced by albite, zeolites, chlorite, clayed minerals (smectites, mixed-layered minerals, hydromicas), calcite. In a lesser measure green tufas are characterized by prehnite and epidote. Horizons of extrusive subvolcanic bodies of dacites and rhyolites accompanied with aureoles of chlorite-calcite or epidote-chlorite propylites and ore mineralization of epithermal or pyrito-polymetallic type. Prehnite and epidote, other minerals of green tuffa, may appear in a lesser measure. These horizons are cutted by subvolcanic bodies of dacites and rhyolites, associated with an aureole of chlorite-calcite or epidote-chlorite

propylites and an epithermal or pyrite-polymetallic mineralization. Supposedly these green tufas arise in island – arc volcanism of contrast – differentiated type in young continental crust owing to activation of seawater, impregnating horizons of pyroclasts at regional warming up of the territory. Warming up is linked with lifting and evolution of mantle diapir, whose final derivatives are acid subvolcanic intrusions. Thus, geologically, these formations are not related to that of propylitized rocks. Most likely, they may be considered as interstitial between products of synvolcanic argilization and regional metamorphism of zeolite and prehnite-pumpellyite facies.

As a matter of fact the family of propylitized rocks, defined above, is characteristic of the orogene stage of crust development in the region of continental margins, island arcs, zones of intercontinental tectono-magmatic activation. Propylitization accompanies conclusive stages of formation of volcano-plutonic associations, comprising granitoid intrusions which have entered the volcanic mass. Usually all varieties of magmatic rocks in a region undergo propylitization independently of the difference in age, but sometimes young dykes are found most of them of basic composition which have entered after propylitization of the mass and are not affected by alterations. Propylitization is not genetically linked with concrete intrusive massifs, but with time it approaches introduction of granitoid porphyric intrusions. This is attested by temperature zoning with increasing temperature towards the contacts and within intrusions up to epidote-actinolite facies.

Mineralization is applied on propylitized rocks usually in the form of intersecting veins or veinous zones, accompanied by periveinous metasomatism of berisitization, adularization and argilization types. The most characteristic aspects of mineralization in propylitized rocks are the lead-zinc, copper-zinc, silver-polymetallic, gold-silver, porphyric copper-molybdenum, etc. In most cases mineralization is a noticeably younger process than propylitization and differs from it by the occurrence of acid metasomatism, which proves properly a peri-ore, periveinous process, only a little forestalling ore deposition. In other cases mineralization appears in propylites in the form of zones of metasomatic sprinkling and veins, such as, for instance, in the Round Mountain mine (Nevada). Zoning of propylites and position of mineralization in them in this deposit is indicated on fig.18.2.

To propylitization are subject tufas of rhyolites of the Round Mountain series (26,7 million years old). Propylitization are replaced by more local processes of adularization, but at the moment of replacement there has deposited a great mass of gold mineralization. Age of this mineralization is less than 2 million years of enclosing tufas [Sander and Einaudi, 1990]. In the given case mineralization was closely linked with propylitization and close to it in time.

Minerals of propylitized rocks. Chlorites in propylitized rocks have an intermediate Mg-Fe composition within the daphnite-clinocllore serie and differs from ore chlorites, which are characterized by high ferruginosity (fig.18.3). Diversity reigns not only in composition but also in structure: propylitic chlorites are formed in structure packets of $I1b\beta97$ type and possess a monoclinic system, but the ore chlorites are built from orthogonal packets of the $1a\alpha90$, $1b\beta90$ types and sometimes instead of them is present berterite (7A-chlorite-like phase). The enumerated varieties of chlorites are diagnosed by X-ray and electron diffractometry analyses. On diffractogram monoclinic chlorites have a noticeable peak of first basal reflection around 14A, with orthochlorites this peak is reduced, but with berthierites it is generally lacking. Correspondences of intensity of peak of the first three basal reflections of the various groups of chlorites is indicated on the diagram (fig.18.4). Electron diffractograms show that the reflexions relative to oblique textures are also different.

Magnesium content of chlorites in association with iron minerals is regulated by sulphur and oxygen fugacity. As a result of thermodynamic calculations [Brindzia and Scott, 1978] in paragenesis with hematite may exist chlorite with a content of not more than 20%, iron, with pyrite not more than 60%, but with pyrrhotite variations of magnesium content of chlorites are unlimited. Additional limitation on the composition of chlorites imposes participation in paragenesis with them of ilmenite or magnetite: with magnetite (with rutile) stable chlorite content is from 20 to 40% ferrous end-member, but with ilmenite, greater ferruginosity up to daphnite. It is possible approximately to estimate the condition of chlorite formation on the diagram of fig.18.5, on which are tentatively indicated the limits of propylitization parameters. It must be taken into account that calciculation of equilibrium composition of chlorites was produced in accordance with reactions with participating andalusite. In natural propylitic associations that mineral is absent, but alumina may get mixed up with albite. This circumstance insignificantly displaces the isolines of magnesianity of chlorite on the diagram at the expense of alteration of free energy of reaction, but the correlation of fugacity is, in principle, not altered. More substantial displacement of composition in the direction of increase of chlorite ferruginosity may anticipate their equilibrium with biotites, but in propylites this is of rather rare occurrence: more often these minerals are found in reaction relations.

Upper T-limits of chlorite stability are estimated on data of [Eugster and Wones, 1958] at 525°C for water pressure of 2 kb with magnetite-hematite buffer, 600°C with QFM buffer and 650°C with MW buffer. Products of chlorite decomposition are quartz- hercynite and magnetite (or fayalite). These parameters have been confirmed by the works of [Turnock, 1960] in which as intermediate products to chlorite synthesis there arise metastable 7A phases.

Their passage to the stable 14A structure of monoclinic chlorite occurred at more than 450°C for the Mg-chlorite and 525°C for Fe-chlorite compositions. At high water pressure (Pt being equal) of 3,5-10kb chlorite decomposed to enstatite, forstetire and spinel at 768-830°C [Fawcett and Yoder, 1966]. On the side of low significance of T the field of chlorite in these experiments was limited by the occurrence of smectite whose quantity increased in the interval between 425° and 350°C. Below these temperatures chlorite was absent. In natural conditions the limits of stability of chlorites varied in the domain of low temperature because of multicomponent natural systems and possibilities of formation of products (e.g. actinolite, biotite and muscovite) at lower temperature than in the experiments.

The limits of chlorite stability depending on the environment's acidity have not been experimentally studied. Geological observations have established that in acid metasomatism Mg-Fe chlorites mix with sericites with subtraction of magnesium more easier than in Fe chlorites, which can be preserved in sericitized rocks. The least pH height may be tentatively to estimated starting from the assumption that chlorite is sericitized with approximately the same acidity as albite. Then at a temperature of 300°C and [KCl]=0.1M [Ivanov, 1973; Khemli, 1965; Zarikov *et al.*, 1976] the acidity index of chlorite decomposition is equal to pH=4.

Epidotes. In the composition of propylitic epidotes are observed high variations of correlation of iron and aluminium from clinozoisite to pistacite. The average height of epidote ferruginosity from low temperature hydrothermal formations amounts to 0.2 [Kepezhinskas & Khlestov, 1971], decreasing in propylites to 0.15, but increasing to 0.35. Manganese epidotes, as a rule, are not formed in propylites: manganese content does not exceed 0.02 formular units. Other admixtures are immaterial. Analyses of epidotes published in literature often contain a small quantity of manganese and alkali which in most cases are made conditional upon pollution of trial by other minerals (usually chlorite, sericite) or poor-quality analysis. K.B.Kepezhinskas and V.V.Khlestov [1971] mention the possibility of limited heterovalent isomorphism of the $2Ca=Na + TR$ or $Ca + Al=Fe + Ti$ type which however with propylitization are practically unrealizable.

The limits of Al=Fe isomorphism in epidotes on geological observation extend to a higher temperature [Miyashiro & Seki, 1958; Kepezhinskas & Khlestov, 1971]. Available information on fields of epidote stability, apparently, are related to the influence on fields of synthesis, to the extent that it strongly depends upon condition and kinetic reaction. So, upper limits of temperature of epidote stability depend upon composition of initial matters in the experiments [Merrin, 1960]: epidote is synthesized from stoichiometric glass mixture $(SiO_2)+Ca(OH)_2+Al(OH)_3+Fe_2O_3$. In experiments with anorthite +wollastonite+ gehlenite+ quartz+water mixture [Myer, 1960] at 2 kb the equilibrium shifts to a

higher temperature, which only decreases with abundance of quartz. K.B.Kepezhinskas and V.V.Khlestop [1971] adduce a crooked expansion of epidote on Ca+garnet+ anorthite + hematite having a steeper slant compared with the preceding data.

About propylitization the lower limits of epidote stability are informative. To which correspond, according to data [Liou & *al.*, 1983], epidote + garnet = prehnite + hematite equilibrium. Between the fields of these parageneses the authors' works mention a "transition zone" in association with epidote + garnet + prehnite which in reality constitutes a domain of metastable transition. Thus, the results of all experiments with epidote participation depend upon kinetically corresponding reactions, which permits to suppose a greater energy of activation of the latter.

Evaluations of stability parameters of natural epidote confirm experimental data on the upper limit of its stability, but indicate a lower temperature of the lower limit. In holes on contemporary geothermal fields formation of epidote is fixed to the minimal temperature of 146°C in depth of 2,2 km (Reikyavik) and 232°C in depth of 450 m (Khveraherdi) [Sidvaldason, 1963], 200°C in depth of 600 m (Vairakei) [Steiner, 1965] and in other regions for temperatures between 180 and 200°C and higher in depths more than 500m. There develop two morphological varieties of epidote, forming in various conditions: 1) prismatic epidote, grain aggregates to which are mixed plagioclase and other calcic minerals and make up veins; 2) needle-shaped epidote in the form of small crystals sparsely disseminated in the rock, principally growing in cavities. The first variety is the usual metasomatic epidote, characteristic of propylites, in equilibrium in the solution. The second variety are metastable skeleton crystals, growing outside the field of epidote stability in case of missing competition with stable phases in free expansion. Epidote, encountered at depth of 0.5 km and less, is related to the second variety.

In the literature are described epidotes occurring in unchanging or little changing magmatic rocks, principally dykes, where epidote forms phenocrysts together with calcic plagioclase, which does not display signs of replacement by epidote [Evans, 1987; Dawes & Evans, 1991; Zen E-an & Hammarstrom, 1982]. This epidote contains a significant admixture of rare earths, and its grains reveal oscillator zoning of R.E. distribution. It forms at 700-800°C, P=7-12 kb and relatively high oxygen fugacity in the region of buffer of biotite+almandine+muscovite+magnesite [Dawes and Evans, 1991]. Formation of such dispersed epidotes is supposedly magmatic. On experimental data, however, the field of epidote stability is separated from fusion by the field of anorthite+garnet+hematite (magnetite) and epidote crystallization directly from melt is possible as unbalanced process, if the activation energy of its crystallization is lesser than for crystallization of a small paragenesis. This

manner of epidote formation displays signs of resorption and is preserved only in conditions of rapid rise of magma and hardening.

Epidote in propylites associates with albite and chlorite; actinolite, biolite and albite; prehnite and albite. In all these parageneses are present, as a rule, magnetite (or hematite, or pyrite) and quartz. Often enough, especially in veins, epidote associates with calcite. Rare enough are associations of epidote with calcic zeolites (mainly with laumontite), which prove metastable to the extent in which between fields of stability of zeolite and epidote there extends a field of prehnite.

Albite, together with chlorite, are the more extended and characteristic minerals in propylitized rocks. Pseudomorph replacement by albite of magmatic disseminated calcic plagioclase serves as petrographic signs of relation of metasomatic rocks to propylitized ones. Sometimes are called propylitized generally peri-ore bleached rocks, composed of quartz, sericite, pyrite, in which may also be present carbonate and chlorite. Essentially, such rocks form as a result of activity of carbon dioxide solutions substantially more acid than the propylitizing, and such rocks are more closely related to the beresitized. In conditions of very small depths (first hundreds of meters) at low temperature the reaction of plagioclase albitization runs sluggishly and plagioclases spread on sericite and carbonate already in a feebly acid surrounding. However, in these condition there form not sericite, but hydromica and other clayed minerals, symbolizing passage to argilized rocks.

Propylitic albite contains not more than 2-5% of anorthite molecules (near intrusive contacts is found oligoclase) and contains practically no potassium (not more than tenths per cent). Albite in average temperature propylites with epidote and actinolite shows a regular Al-Si distribution in structure, which characterizes “lower” albite, and has a positive angle of $2V = 60-70$. Its crystals are polysynthetically twinned according to albite law. In low temperature near-surface propylites albite is characterized by an irregular Al-Si distribution, a great negative angle (of) $2V = 70-80$, which is characteristic of “high” albite, and is feebly twinned, or not at all [Rusinov, 1972]. The degree of twinning is on the whole correlated with that of the mineral’s structure regularity. Irregular albite appears as intermediate metastable product of plagioclase albitization, and with time or under thermal influence it passes to a stable regular form at low temperature.

Albite associates with chlorite, epidote, actinolite and calcite. Around quartz-ore veins it gets reinforced by sericitization, but in the stage of “advanced propylitization” is replaced by adular.

Actinolite is present in propylitized rocks in facies of increased temperature in endo- and exocontacts of prophyric granitoid intrusions. It is represented as an intermediate member of the tremolite-actinolite series with 20-50% ferruginosity. Ferruginosity variations are determined by the composition

of initial rocks and the temperature (with temperature increase there is a tendency to formation of less ferrous varieties). As a rule, the mineral does not contain aluminium or sodium except its appearance at relatively high temperatures at the level of the temperature at the boundary with epidote-amphibolite facies. Magmatic pyroxenes and amphiboles are replaced by actinolite. Sometimes is observed replacement of chlorite by actinolites, which corresponds to the progressive type of propylitization development. More often, on the contrary, actinolite is replaced by chlorite at the regressive stage of the process. In equilibrium with chlorites actinolite is not observed in propylitized rocks.

Actinolite associates with epidote and albite, or with biotite and albite-oligoclase. In both cases there exist, moreover, quartz and magnetite (or pyrite). At peri-ore metasomatism actinolite is replaced by sericite, but usually chlorite is formed as intermediary product.

Biotite. In propylitized rocks greenish biotite is frequent with pleochroism from dark greenish on p_g to light-greenish on p_p . It extends in deep zones of propylitization, near contact with magmatic bodies. Colouring of biotite appears with low content of titanium (0.1-1.5% ToO_2) and increasing content of ferrous oxide (up to 19% FeO). In the vicinity of magmatic contact there increases in the biotite composition the titanium content (up to 4%) and decreases magnetite with 0.5-0.7 to 0.3-0.4 (relation of magnesium to the sum of magnesium and total iron). Colouring biotite also changes from greenish to red-brown with pleochroism from bright red-brown to light red-brown. Brown biotites with relatively high titanium content are formed also with propylitization of terrigenous rocks (quartz-muscovite-chloritic-schist) also far from intrusion.

Biotite in propylites associates with quartz, orthoclase, magnetite, actinolite, epidote. However, epidote is often subject to replacement by biotite or by biotite and amphibole. By biotite are also replaced chlorites, muscovite, at places pyrite. In biotitized rocks there is commonly enough development of small scale biotite on albitized phenocrysts of plagioclases. In most cases biotite scales are disseminated in the rock, but there occurs condensation and metasomatic veins. In a zone of magmatic contact there may arise biminerall orthoclase-biotitic rocks. Are also found biotite veins with tourmaline. Around quartz ore veins biotite is replaced by sericite.

Biotitization is accompanied with entry in the rocks of magnesium, iron and potassium and removal of calcium. Apparently, the process is brought about by solutions of increased alkalinity compared to the condition of epidote-chlorite propylitization. Paragenesis with tourmaline and presence in the biotite's composition of fluorine in 0.15-0.20% quantity testifies to increased activity of volatiles (F,B) in the propylitized solutions.

Associations of minerals, facies and physico-chemical conditions of propylitization. Propylites contain minerals precipitated from solutions, and relicts of solution minerals of the initial rocks. So, usually propylites are formed of an unbalanced mineral association; therefore their mineral composition may be represented in the form of pellets newly formed minerals ($n\%$)/relicts ($r\%$) where n and $r(\%)$ indicate content of newly formed minerals and relicts in the rock. In feebly intense propylitization there do not always occur “definitive” propylite minerals. For instance, in outer zones of propylitization olivine and pyroxenes are replaced by serpentine with quartz, while plagioclase is preserved in these zones. As far as the process is reinforced, plagioclase is replaced by albite and calcite, but liberated alumina reacts with serpentine, producing chlorite. Like pyroxenes, plagioclases are unstable in propylitization; therefore relative preservation depends only upon the kinetic reaction of the replacement. This example shows that precisely the chemical kinetics determines in a given case the pace of the process, and propylitization may occur in a kinetic domain.

With intense metasomatism in conditions of increasing temperature (250-300°C) propylitization leads to complete replacement of magmatic minerals by newly formed, in equilibrium with hydrothermal solutions, i.e. to formation of parageneses of minerals of propylites. Parageneses of minerals in propylitized rocks depend, grosso modo, upon composition of initial rocks, temperature and activity of magnesium and potassium. With metasomatic replacement of acid rocks is formed a quartz-orthoclase-epidote facies with a small quantity of chlorite with increased ferruginosity. At the same temperature there forms on andesites a chlorite-albite-epidote facies. A distinction is defined by low content of magnesium in acid rocks with inertia of its component in the propylitization process. Another distinction is linked with formation of potassium feldspar instead of albite. Usually potassium and sodium are mobile in metasomatism of the mentioned type, but, apparently, potassium shows inertia in case of rocks initially enriched in it. Somewhat different conditions accompany adularization in propylitized rocks, when adular develops on propylitic albite forming earlier at the stage of “advanced” propylitization. Later adularization is possibly linked with alkalization of a hydrothermal solution as a result of boiling up in small depth with withdrawal of acid components in gaseous phase.

The main facies of propylitized rocks depending upon temperature and magnesium activity are indicated on fig 18.6. The diagram is qualitative, the boundaries of the facies field correspond to monovariant equilibria, for all of which there do not exist thermodynamic data. With increasing T the albite-calcite facies is replaced by an epidote chlorite, but then by an epidote-actinolite one. In the epidote actinolitic facies in albite calcicium content increases to 5-10% of anorthite molecules, which corresponds to a temperature about 300°C. To a further temperature growth corresponds an albite-actinolite facies. Growth of magnesium activity brings about reactions of biotitization and formation of

biotite-actinolite facies, which usually borders on contact hornfels of diopside-orthoclase-phlogopite or diopside-orthoclase facies. Appearance of a biotite-actinolite facies in a deep rear zone of propylitization is linked with mobility of magnesium and its addition to magmatogene solutions. In portions of intense biotitization by these minerals are replaced not only chlorites, but also albites, are formed nests and veins of monomineral biotite, or biotite in paragenesis with actinolite and epidote. As a rule the main mass of mineralization extends above the limits of the actinolite facies, in lower temperature epidote chlorite propylites.

As agents of propylitization serve solutions formed from two sources or more. A portion of magmatic fluids is remarkable by the high activity in them of magnesium and potassium, which makes conditional magnesian or potassic trends to propylitization (biotitization or adularization, respectively). Together with magmatic in hydrothermal solution indubitably exist also water components buried in the thickness of the rocks undergoing propylitization. This follows from an enormous volume of propylitized rocks in hundreds of cubic kilometers, but also from data on oxygen isotopy. Instructive instances of mapping of distribution of oxygen isotopes are found in rocks of some ore districts. A gold –silver deposit of Bohemia (Oregon, E.-U.) included in propylites is formed at the expense of andesites and dacites. In unchanging volcanites distant from the ores the value of $\delta^{18}\text{O}=6\text{‰}$, but in propylitized rocks near the ore zones this value decreases (fig.18.7) more than 10, attaining in ore zones negative significance up to $-4\ \delta^{18}\text{‰}$. Apparently, in hydrothermal solution a significant share consists of waters of meteoric origin. Analogous data are obtained for the sulphidic gold-copper deposit of Kizilbulak in Azerbaijan [Gavriluk et al., 1991].

In propylitized submarine masses mixed with pyrite deposit, a significant part of hydrothermal solution consists of sea water the presence of which is proved by correlative values of D and O, near to those in sea water. There exist quantitative estimations of the share of magmatic components in a hydrothermal ore-forming solution, but concerning propylitized solutions there are not sufficient data.

A comparison of adduced data on the conditions of synthesis and stability characteristic of propylitic minerals with the data on the study of contemporary volcanic hydrotherms and thermodynamic calculations permits to evaluate the extent of the conditions at which propylitization occurs. The general temperature interval of propylitization is situated near 200-350°C; for albite-calcite-chlorite facies, 200-250°C; for epidote-chlorite, 250-300°C; for actinolite-epidote, actinolite-albite and biotite-actinolite facies, higher than 300°C. Estimations of composition of propylitized solutions are few in the literature. Research on fluids of an inclusion in adular from propylites, mixed with the gold deposit of Round Mountain (Nevada), and thermodynamic calculations [Sander and

Einaudi, 1990] have shown a low salinity of propylitized solutions (0-0.2% equivalent NaCl), proximate to the neutral alkaline value pH=7-7.5 at 250°C, potassium concentration in the order of 10^{-3} M. Ore deposition in these propylitized solutions is linked by the authors with the concluding stage of propylitization, in which a typical propylitization gives way to adularization. Later adularization is caused usually not only by growth of potassium activity as far as through temperature decrease and in its influence by growth of relative potassium activity and sodium activity in the solution. Propylitized rocks in formation of synvolcanic argillites are formed in a more acid environment (pH=5,5-6,5).

Propylitization and mineralization. Propylitized rocks forming in border facies in ensembles of synvolcanic argillized rocks and in acid periveinous metasomatites, as a rule do not contain ore concentrations. Ores in these objects are concentrated in outer metasomatic zones of maximally transformed rocks. Propylitized rocks forming independent ensembles (of propylitized formation), mix with mineralizations of various types: stannous, lead-zone, silver-polymetallic, gold-copper, gold-silver etc. Ore bodies may have the form of intersecting veins, zones of veins, vein- interspersed zones. Usually easily come to light signs of later ore formations in relation to propylites [Vassilevsky, 1970]. As such signs serve, for instance, depositions of peri-ore acid metasomatism on mineral associations of propylites and intersection with ore bodies of boundaries of propylitic facies. Intersections depositions we generally characteristic of lead-zone and most gold-silver ores. Deposition determines extended correlation for disseminated (vein-interspersed) mineralization, but also in this case it is usually accompanied with local peri-ore metasomatism, deposited on propylitized rocks.

A special case is dissemination of gold or gold-silver mineralization in adularized propylites. Judging from described Transylvanian gold-silver deposits [Giusca, 1945] and gold deposit of Gold Mountain in Nevada [Sanders & Einaudi, 1990], adularization immediately continues the propylitization process, manifesting its conclusion. Gold deposition with accompanying ore minerals occurs simultaneously with formation of late adular, with which the contour of industrial gold content occupies a predominant part of the volume of propylitized rocks and does not trespass their limits (fig.18.8). The conditions of ore formation in that case, according to the cited authors, practically coincide with the conditions of propylitization. This means that propylitizing solutions contain soluble gold and other metals, but their condensation results from temperature fall and variations of acidity-alkalinity of the rock.

For the deposition of tin [Razmakhnin & Razmakhnina, 1964] and gold [Russinov, 1989] is noticeable a limited deposition of ore bodies in zonings of propylitized rocks. Tin mineralization coincides fundamentally with the biotite facies in the roof of a granitoid massif, but gold mineralization

concentrates above the limits of the biotite facies with the epidote-chlorite surrounding it.

From the adduced analysis of geological setting and the conditions of formation of propylitized rocks it follows that a characteristic feature of propylite formation is its occurring in volcanic masses as a result of a hydrothermal process linked with entry of a porphyric granitoid intrusion of increased content of alkalimetal. In the formation of propylites occurs a metasomatic zoning: the rear zone, contiguous with contact hornfelses, is deposited in a biotite-albite-actinolite facies and is characterized by addition of magnesium; above is placed an epidote-chlorite facies with linear zones of epidotes and portions of epidote-actinolite facies. Similar deposition and zoning are precisely characteristic of ore- bearing propylitic fields.

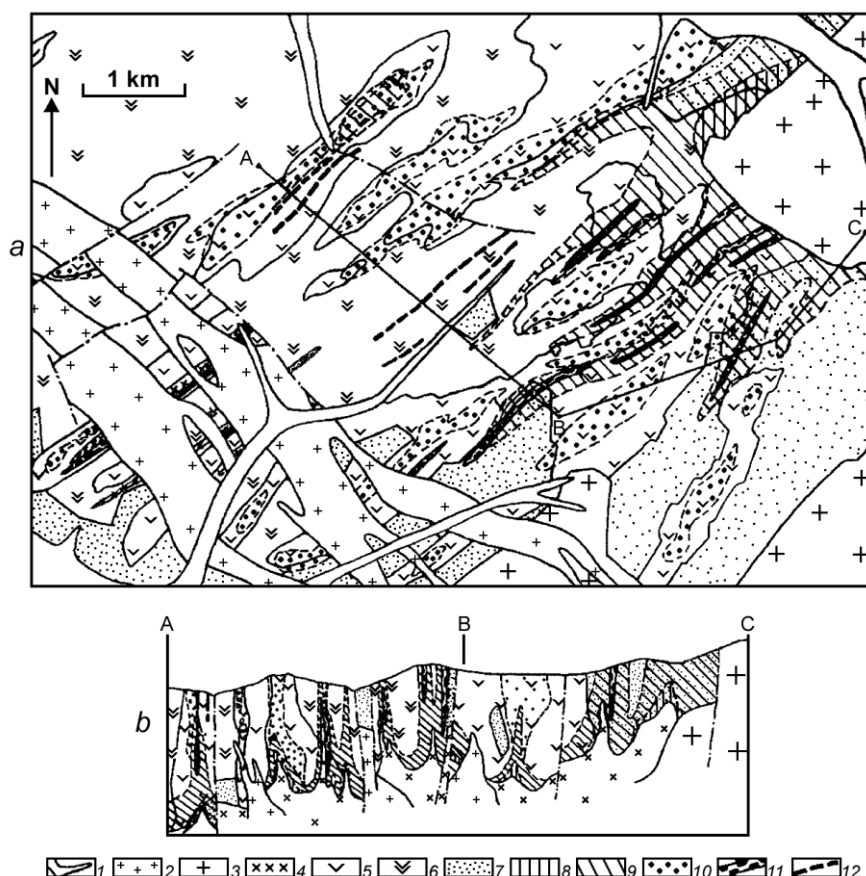


Fig.18.1. Outline of expansion of metasomatic facies in ore-field of the Mnogovershine deposit (Lower Amur) [Rusinov, 1989].

a- plane; *b*- cross-section through line A-B-C; 1-alluvium, 2-granodiorite-porphyrries, granite porphyries and syenite porphyries of phase V intrusion; 3 – granodiorites and syenitodiorites of phase IV intrusion; 4 – alkaline granodiorite porphyries of phase IV intrusion ; 5-6 – andesito-dacitic volcanic formation (5-subvolcanic and crater facies; 6-mantle facies), 7 – aleurolites and sandstones, 8 – contact hornfelses; 9-10 – facies of propylite (9-biotitic, 10 epidote-chloritic), 11– peri-veinous beresites with quartz-ore veins; 12 – zones of supra-ore metasomatic veinlets of altering rocks.

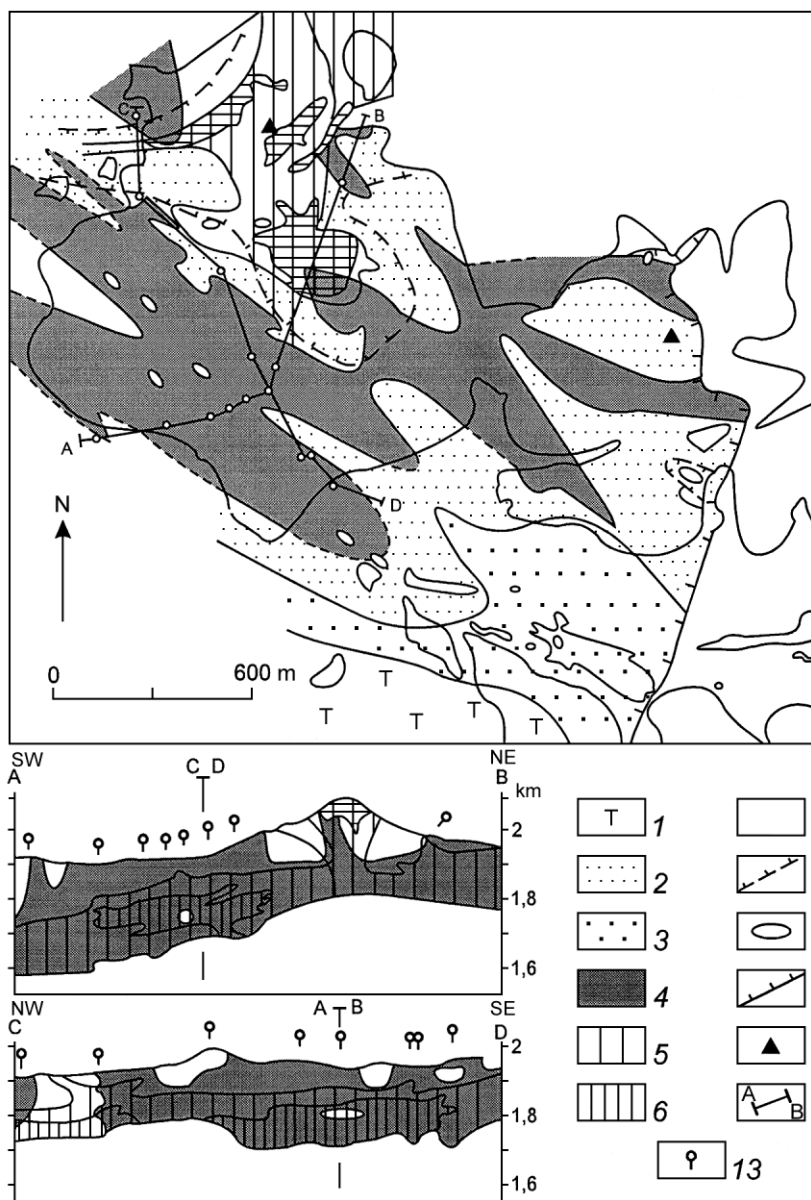


Fig. 18.2. Extension of metasomatic facies in ore-field of Round-Mountain after [Sander and Einaudi, 1990].

1 unaltered tufa-rhyolites; 2-4 propylitized rocks with various degree of replacement of magmatic plagioclase by adular or albite (2-initial replacement; 3-medium degree; 4-complete replacement; 5-6- adularized rocks with adular content < 100% (5) and = 100% (6); 7-intensively silicified rocks; 8-limits of argillization; 9-limits of quaternary deposit; 10 - lower limit of expansion of tufas of the Round-Mountain formation; 11-triangulation points; 12-lines of cross-sections and boring holes on the plane; 13-position of boring holes on cross-sections.

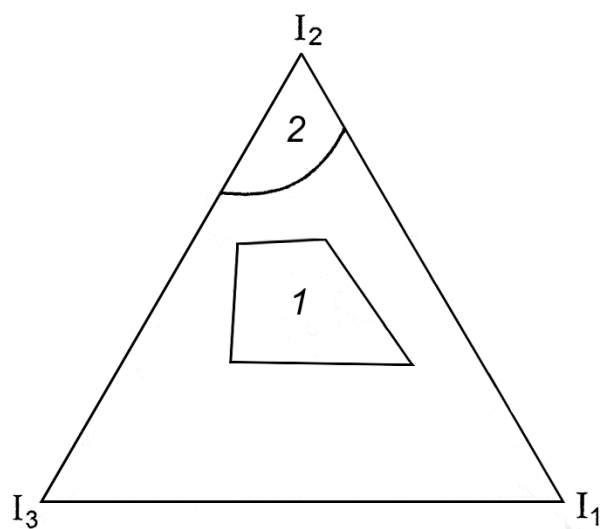
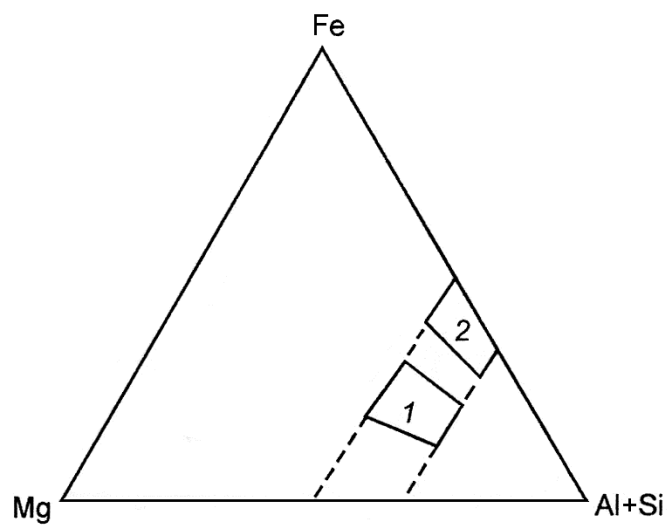


Fig. 18.3. Composition fields of chlorites from propylites (1) and synore metasomatites

Fig. 18.4. Rates of intensity of the first three basalt reflections of chlorites from propylites (1) and synore metasomatites (2).

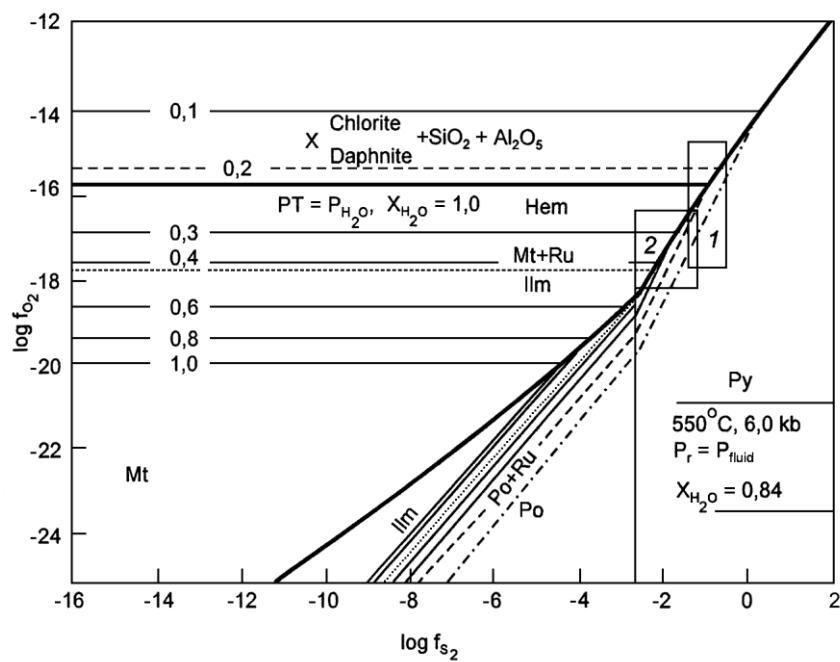


Fig.18.5. Dependence of ferruginosity of chlorites upon fugacity of sulphur and oxygen [Brindzia and Scott, 1987].

Denotation by rectangles of the field of chlorites from propylites (1) and from ore-accompanied metasomatites and ore veins (2).

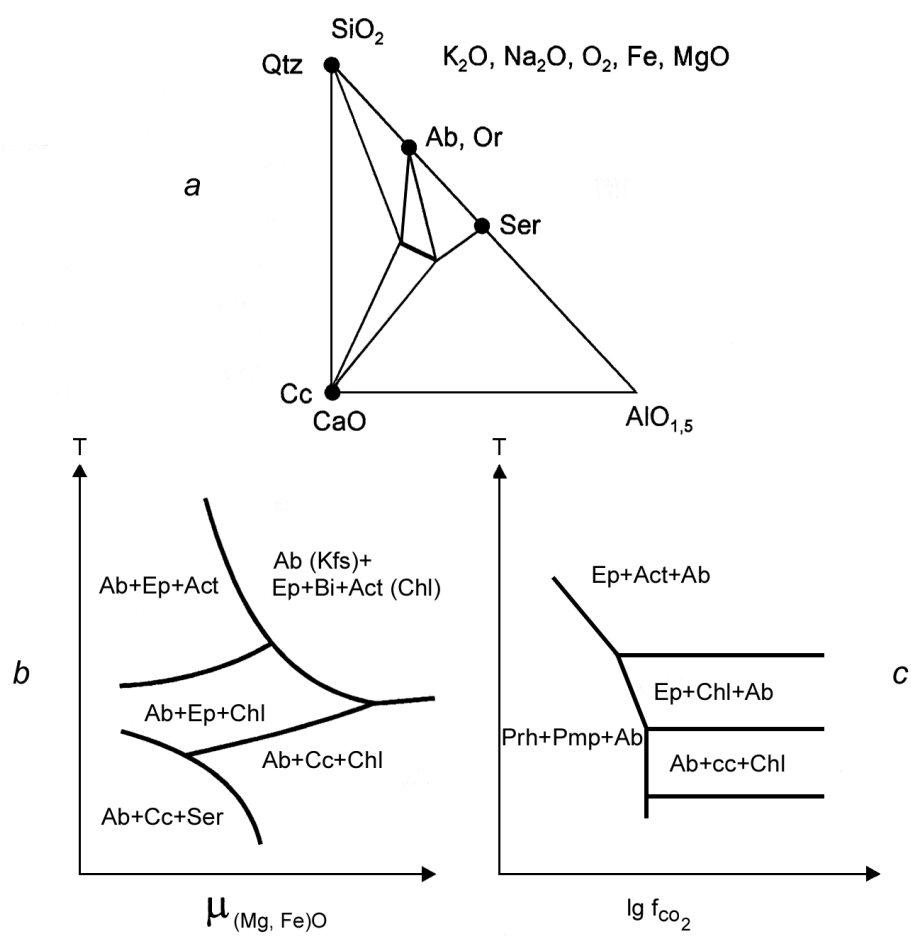


Fig. 18.6. Parageneses (a) and facies (b,c) of propylites formed at mobile behavior of magnesium and iron.

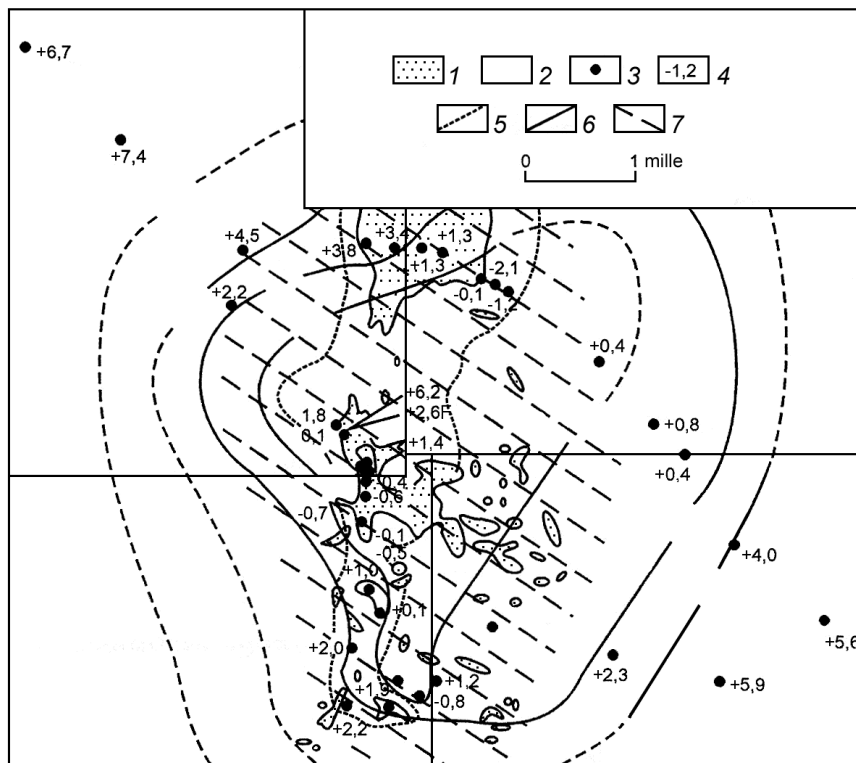


Fig. 18.7. Schematic map of ore field of Bohemia (Oregon, USA) with isolines of isotopic composition of oxygen of enclosing volcanic rocks [Taylor, 1977].

1–intrusive diorites; 2–volcanic rocks; 3–sample locations; 4– $\delta^{18}\text{O}$ values; 5–limit of contact-metasomatic aureole; 6–isolines of $\delta^{18}\text{O}$; 7– propylized rocks.

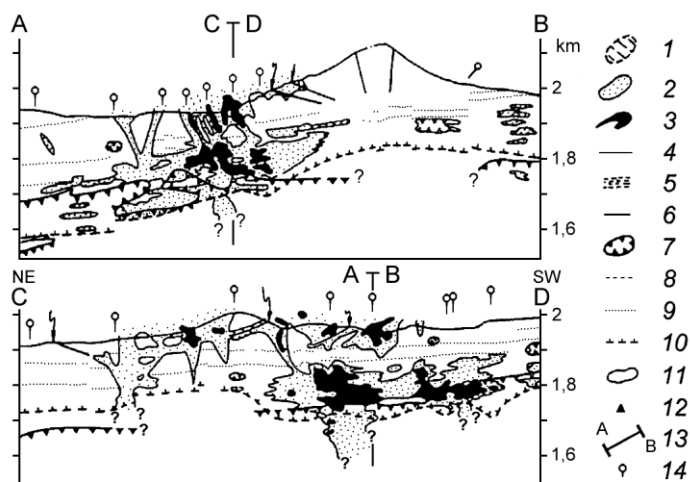
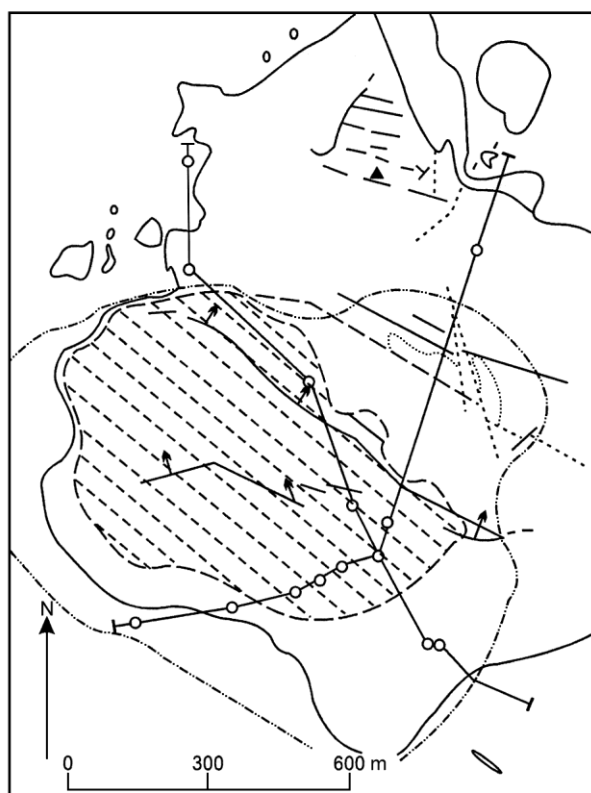


Fig. 18.8. Distribution of gold in propylitized rocks of the Round-Mountain deposit [Sander and Einaudi, 1990].

1-3 aureoles of various gold content (1: $\geq 0,72$ g/t; 2: 0,38-1,42 g/t; 3: $\geq 1,41$ g/t); 4- steep sloping mineralisation fractures; 5-old outputs; 6-gently sloping veins previously exploited; 7-limits of non-oxidized sulfides and carbonates; 8-main fissures; 9-contacts of rocks; 10-lower limit of extension of tufas of Round-Mountain; 11-limits of alluvium; 12-triangulation points; 13-position of drill holes on map; 14-position of drill holes on fractures.

Chapter 19

Secondary quartzites

Definition. Secondary quartzites (SQ) are substantially quartzic rocks (quartz content 50-100 vol.%) formed through metasomatic silicification of initial rocks of various composition. The term was first proposed by E.S.Fedorov. A further elaboration of this notion can be found in the works of M.P.Russakov, D.S.Korzhinsky, N.I.Nakovnik. The term is not used in English language literature, where it is not admitted to isolate the corresponding specific types of metasomatic alterations, but to utilize concrete designations of altering rocks (corundic quartzites, andalusite-quartz rocks, alunite-quartz rocks). The framework of the term “secondary quartzite” is defined conventionally enough, since a process of silicification may be linked with the influence of acid solutions, compositions, temperature and geological setting which strongly vary. Rock silicification is typical of greisenization argilization and quartz-sericitization processes of rock alteration, in which quartzic cores sometimes present rear zones of metasomatic columns.

The term SQ has also aroused objections amongst Russian geologists. They proposed to replace it by “metasomatic quartzites” or “hydrothermal quartzites”, but these changes were not accepted in the literature. Unlike the designation of rocks and metasomatic facies, the term SQ, apart from a specific mineral composition and physico-chemical parameters, implies a particular geological environment for the appearance of the metasomatic process. Amongst the geological situations in which SQ is found, most typical are the fields of development of medium-acid volcano-plutonic components in active continental margins and on insular arcs at orogene stage of development. Silicification process have a distinctly deposit character and are related to the postmagmatic stage. Most SQ appearances are linked with porphyric magmatism of hypabyssal-subvolcanic facies. D.S.Korzhinsky, after E.S.Fedorov and M.P.Russakov, have related to SQ postintrusive metasomatic rock silicifications in apical parts and roofs of porphyric granitoid massifs. N.I.Nakovnik has widened the notion, introducing into it products of solfatar processes in near-surface conditions on volcan. Some researchers of epithermal

deposits have scrutinized zones of quartz, quartz-alunite, quartz-kaolinite composition in periveinous metasomatites as well as SQ. Similar widening of the form are explained by the similitude of mineral composition of the scrutinized zones, but they lead to the unification of the genetically various formations, which contradicts the formation approach. Solfatar alterations, quartz “hats” and zones of silicification on epithermal deposits form zones or facies in composition of a complex of solfatar-argilized or periore-argilized rocks, i.e. no geological independent formations appear, and only as facies of argilizitic formation.

As the main mineral SQ appear quartz, sericite, pyrophyllite, alunite, kaolinite, dickite, andalusite, corundum, fluorite, rutile, diaspore, pyrite, hematite. Often are found dumortierite, zunyite, topaz, lazulite, turmaline, geikielite, svanbergite.

Basic mineral equilibria for SQ may be described in the framework of the Al_2O_3 - SiO_2 - H_2O systems, which was studied by V.A.Zharikov *et al.* [1972], [J.Hemley *et al.* 1980]. Moreover, interest was later directed to studying the solubility of oxid alumina and alumino-silicates Al_2O_3 - H_2O , Al_2SiO_3 - H_2O systems [Korzhinsky 1987, Ostapenko *et al.* 1987].

Specific paragenes of SQ are diaspore-pyrophyllite-corundum+andalusite, zunyite-diaspore, alunite-pyrophyllite. In most of them quartz may be present, although usually the enumerated minerals are found in later silicified rocks and may be in unbalance with the quartz. In particular, this proves to be corundum [Korzhinsky, 1963, Popov 1977].

So, analysis of geological deposits, of mineral composition and ore mineralization in intensively silicified rocks permits to distinguish among them a few genetic types (table 19.1), including strictly SQ, in the interpretation of E.S.Fedorov and D.S.Korzhinsky, and facies of silicification of rocks in argillizite formations.

Table 19.1. Genetic types of products of silicification.

Metasomatic formations	Deposits	Paragenesis of main facies of replacement	Type of mineral
Secondary quartzes	High-aluminous Porphyric	Qtz – Crn Qtz – Ser – Py	Al Cu, Mo, (Au)
Advanced argillisites	Epithermal Pyritic	Qtz – Alun – Kln Hydromicas	Au, Ag, (Cu) Cu - Zn

Secondary quartzites linked with corundum mineralization. An outstanding specimen of development of high alumina mineralization in silicified rocks is the deposit of Great Semis-Bug (Central Kazakhstan). SQ on

the deposit forms in connection with hercynian acid magmatism. Magmatic rocks are present in a complex of rhyolites, their tuffs, subvolcanic dykes and stocks of granite-porphyrines.

The greatest development amongst metasomatic rocks is that of silicified varieties. N.I.Nakovnik [1964] has defined a few fundamental mineralogic types of SQ: sericitic, monoquartzitic, sericito-andalusitic, alunitic, andalusitic (SQ types are numbered in the order of diminution of their relative expansion). Corundum SQ are not divided in independent types, since corundum is exclusively localized in central parts of the deposit, where it forms a sprinkling and small veins in other SQ types. On the plan (fig.19.1) the most extended sericitic SQ constitute a general background of metasomatic alterations. Monoquartzites form a thick vein-like, steeply dipping body composing the massif of the Great-Semis-Bug mountain. The quartzic body divides the SQ massif into two parts, controlling SQ distribution in extension: an inner corundum-andalusitic and an outer one with alunitic mineralization.

A characteristic feature of monoquartzites is the presence in them of a relict structure of quartzitic porphyry and sprinklings of unalterable initial quartz. This testifies to the fact that monoquartzites do not appear in vein fulfillment but are formed metasomatically. This is indicated by the gradualness of transition from monoquartzites to other SQ types: sericitic, andalusitic and alunitic.

Amongst secondary quartzites are found high aluminiferous mono- and bi-mineral rocks. Their morphology is varied: veins, nodules, mineralized nests and steeply dipping lenticular deposits. The largest of them, an andalusite-corundum deposit, a body 160-180m long, with thickness of 40m at the utmost, has an asymmetrical, funnel shape. Judging from data of geological works, the deposit is steeply subparallel to the incidence of the monoquartzite body. The core of the deposit is in a corundum rock bordered by a thin andalusite corundum shell. The outer zone consists of andalusite-sericite SQ varying in composition. K.I.Astashenko has established a vertical zoning in the structure of the core. The corundum body of the upper part contains hematite, rutile and barite, in depth they are represented by pyrite-muscovite-corundum rocks, which further down are replaced by small grain pyrite-corundum rocks.

Corundic bodies have a taxitic breccia texture and possess a significant porosity, up to 10-12% [Nakovnik, 1964]. In the mineral composition predominates corundum (72-95 vol.%), andalusite (2-5 vol.%), sericite (7 vol.%), are present rutile, pyrite, diaspore, topaz, barite. Corundum develops later than basic SQ minerals, and therefore testify to corrosion correlation of corundum by muscovite and andalusite, but there are also present nodules of andalusitic and sericitic SQ, cemented by corundum. At places gross crystal corundum associated with rutile and barite form thin branching veins, intersecting grayish thin-grained corundum rocks.

Many features of geological structure of the SQ massif of Semis-Bug, in the opinion of N.I.Nakovnik, testify to the fact that SQ is localized in central parts of volcanic apparatus. This is indicated by signs characteristic of volcanic centers: abundance of volcanic tuffs, bombs and breccias, steep sinking structures of elements in lavas, arc-shaped deposits of quartz, developed, probably on a system of contraction cracks and collapses at caldera formation.

Secondary quartzites linked with deposits of porphyry type. Processes of silicification on deposits of porphyry type are widely spread and represent the result of acid metasomatism of quartz-feldspar, quartz-sericitic (phyllitic) and argillitic types. To porphyry metallization are habitual the many stages of hydro-thermal process and, respectively, some stages of SQ formation. A detailed description of the development of silicification processes can be found for the deposits of Island-Copper, San Manuel, Butte, Kunrad, Kalmakkir, Assarel [Popov, 1977]. V.S.Popov [1977] remarks that SQ represent inner or upper parts of porphyry bodies, linked with the products of “advanced argillization” and with phyllites. The complexity of interactions with complexes of SQ was also pointed out by V.L.Rusinov [1989], who defined appearance of SQ in conditions of porphyry deposits or as intermediary metasomatic zone between quartz-feldspar and quartz-sericite metasomatites, or as inner parts of argillite aureoles. In this way, processes of silicification and development of high alumina mineralization (andalusite, corundum) in time get detached from the appearance of potassium metasomatism (Qtz-Or, Qtz-Bi). An example of SQ development linked with porphyry types of mineralization is to be found in the copper deposit of Kunrad in Kazakhstan [Gasisov, 1957; Nakovnik, 1968; Udin, 1969] and molybdeno-porphyric Climax in USA [White *et al.* 1984].

The Corundum deposit is confined in a stock of granite-porphyry, an intruding patch of effusives. Metasomatic alterations and metallizations are precisely controlled by a body of granite-porphyries. A vertical zoning has been determined in the distribution of metasomatic rocks. The inner one (deepest zone, about 100m thick) is represented by propylites (or potassic propylites [Popov 1977]), in which initial intrusive rocks are replaced by Bi+Chl+Ep+Ab+Py(+Or) association. Above the quarry a transition is established to strongly silicified rocks. Transition from propylites to SQ occurs in an interval of about 10m. Here associations with kaolinite and sericite are close in composition to argillites.

Strongly silicified rocks constitute the main part of the metasomatites in the deposit. According to N.I.Nakovnik [1968] estimate the vertical scale of their development amounts to no more than 400-500m. Amongst them the most spread are sericite-quartz rocks. Andalusite-sericite types develop exclusively on acid lavas in close contact with stocks of intrusive rocks, formed in an extended structure, recalling contact aureoles. In the zones of andalusite-sericite quartzites is recorded the development of high-potassic mineralization: pyrophyllite,

corundum, alunite. Sericite-quartz rocks consist of quartz (30-60 vol.%), sericite (40-50 vol.%), pyrite and rutile. SQ, developed on intrusive rocks, are characterized by abundance of thin quartz veins, intersecting the altered rock.

Unlike apointrusive varieties, in apovolcanic SQ, as a rule, such veins are not observed, and silicified rocks even preserve signs of flow structure of initial lavas. Transition from sericite-quartz rocks to andalusite-sericite is gradual, with varying quantitative correlations of the minerals. Andalusite content varies from 5 to 80 vol.%. The interrelations of sericite and andalusite are contradictory: they are observed as signs of combined growth as well as corrosion correlation. In tight association with andalusite develop alunite, dickite, pyrophyllite, diaspore and corundum. Judging from the interrelations, these minerals, except corundum, have formed on concluding stages of SQ formation at declining temperature. Corundum also forms after andalusite crystallization and is observed in the aspect of idiomorphic crystals developed on porphyroblastic andalusite. Judging from the absence of corundum-alunite, corundum-pyrophyllite association, etc., corundum is formed at an independent stage. This is also indicated by the distinctly extended control of distribution of andalusite-corundum SQ facies, exclusively concentrated in the inner parts of andalusite rocks. A similar picture of development of the process of silicification and high potassic mineralization is observed on the copper-porphyrific deposits of El Salvador [Gustavson & Hunt, 1975]. Here development of quartz-sericite metasomatites (phyllites) have preceded formation of potassic (orthoclase-biotitic) metasomatites. In the inner parts of the phyllite aureole develop andalusite-quartz metasomatites, where in the form of single finds is recorded corundum, replacing andalusite. Later, with declining temperature, in argillized rocks are formed pyrophyllite and alunite. On the El Salvador deposit phyllitic type of metasomatism is linked with formation of pyrite-bornite mineralization.

Ore mineralization on the Kunrad deposit is tightly linked with processes of silicification. Veinous and sprinkled mineralization (chalcopyrite, pyrite, galenite) develops in quartz-sericitic rocks. At the same time most copper-porphyrific deposits show extinction of the extent of mineralization in the zones of highest acidity of leaching [Popov, 1977].

SQ linked with pyrite ores. SQ were first distinguished as independent types of alteration by E.S.Fedorov and V.V.Nikitine on the Ural pyrite deposits. Later on SQ in the Kaban pyrite deposits (Northern Ural) were described in detail by V.P.Loginov [1951]. Similar types of zoning were described in the deposit of Chizeuil (France) [Lemiere *et al.*, 1986], where SQ replace sulphide deposits, built with pyrites and sulphides of copper with accessory gold.

Sulphide bodies in SQ of the Chizeuil deposit has the form of lenses, and they show tendencies to forming massive deposits, stockwerk bodies. They are surrounded by bright quartz-andalusite rocks, with numerous intersecting pyrite veins. The initial rocks present subvolcanic dacites. The structure of

metasomatic quartzites is variable: massive in sprinkled pyrite and muscovite; banded (the zones alternate, enriched either in quartz or in andalusite); jointing, with separation, parallel extension of sulphide bodies; breccia-like containing fragments of massive ores, in their turn cemented by sulphide cements. Mineral composition and zoning of metasomatic alterations are presented on table 19.2. Metasomatic alterations around sulphide bodies in the Kaban deposits are, on the whole, similar to those of Chizeuil, but differ in developing corundum in quartz-andalusite rocks and presenting fluor minerals (topaz and fluorite) in the frontal parts of the aureoles, surrounding sulphide pipes [Loginov, 1951].

Silicified rocks are described in metasomatic aureoles of sulphide bodies on pyrite deposits of Chypriot type [Richards *et al.*, 1989] in the region of pyrite deposits of Bulgarian and Yugoslav Central mountains (Chelopech, Elshitza, Kracen, Bor, Maydanpek)[Radonova & Velinov, 1974].

Silicified rocks in epithermal deposits. The wide development of silicification processes is characteristic of acid sulfatic (or, in another terminology, high sulphidized) type of epithermal deposits [Herald *et al.*, 1987], linked with the development of argillization in them. Silicification, as a rule, represents formation of ore bodies. Such correlations are established, for example, on epithermal deposits in the province of San Juan Mountain (Colorado, USA), where are well known some big deposits of noble metals such as RedMountain Pass and Summitville. Silicified rocks of this type are related by American

Table 19.2. Mineral composition and zoning of metasomatic alterations in bodies of secondary quartzites of Chizeuil (Morvan, France) [Lemiere *et al.*, 1986]

Massive sulfide bodies	Secondary quartzites		Adularized dacites	Initial dacites
	Zone 1	Zone 2		
Quartz Andalusite Kaolinite Pyrite Chalcopyrite Enargite	Quartz Andalusite Kaolinite Muscovite Pyrophyllite Diaspore Corundun Rutile Pyrite	Quartz Feldspar Muscovite Rutile Pyrite	Quartz Albite Adular Muscovite Chlorite Biotite Rutile Sphene Pyrite	Quartz Oligoclas Albite Chlorite Sphene

geologists to products of “advanced argillization”.

The Summerville deposit has been studied in full detail by [Stoffregen, 1987]. Intrusive rocks in the deposit are represented by quartz dacites (fig. 19.2).

They burst patches of andesites and rhyodacites formed in aggregates of cauldron complexes of lava.

The youngest eruptive rocks of the region are represented by subvolcanic bodies of rhyolites of Grosny Mountain. The deposit is confined to a zone of fracture intersecting a complex of cauldron formation, and gravitates to a contact of lava with massive quartz latites. The structure of the deposit is represented by numerous extended mineral zones of north-western and northern course. Their deposition is controlled by the position of contacts between intrusive phases of quartz latites and between quartz latites and rhyolites.

Hydrothermal peri-ore alteration of rocks occupies a well defined zoning. Inner parts represent nearly pure quartz ("cavernous quartz") and are surrounded by zones of quartz-alunite, illite and montmorillonite composition (fig. 19.3a).

In the zone of "cavernous" quartz arises a leaching of all rock forming minerals, and it is composed of quartz, sulphides, second generation anatase and zircon. Silicified rocks form irregular tubular bodies from a few centimeters to 70m thick, deposited at a depth of 100-200m (fig. 19.3.6). The morphology of the quartz distribution is varied: the basis consists of very fine-grained aggregates (grains from 10 to 100 microns). They contain great relicts of sprinkled magmatic quartz, preserved through metasomatism, and other quartz formed in cavernous cavities. In interstices of fine-grain quartz are formed pyrite and anatase. In cavern quartz stand out portions of massive structure, lacking in voids. The distribution of such portions in the limits of the zone is accidental.

A quartz-alunite zone either shows itself as very internal, or borders with a quartz kern. Mineral composition of the zone: quartz, alunite, individual grains of svanbergite. Quartz and alunite form a very fine-grained mass (grains of 100-250 microns). Alunite contains 10-25% of Na molecules. From ore minerals pyrites are usually knitted with alunites. Are present in small quantities covellite and native sulphur. In the outer parts of a quartz-alunite zone develops an association of quartz+alunite+kaolinite, with a thickness from a few centimeters to one meter. This paragenesis is transient to a zone of illite alteration.

The inner zones have a sharp contact with more outer illite and montmorillonite-chlorite zones of hydrothermal alteration. Mineral composition of the illite zone: quartz, illite, with a subordinate quantity of montmorillonite and kaolinite. Of ore minerals predominate pyrite on biotite, and are registered as of second generation chalcopyrite, galenite, sphalerite and covellite. The illite zone of alteration in the direction of lateral mineral gradually turns into montmorillonite-chlorite, built of smectite (mostly, montmorillonite), pyrite, Mn-chlorite, carbonate. This zone is replaced by feebly altered quartz latites. Fresh latites are represented by porphyric rocks with phenocrystals of potassic feldspar, plagioclase, biotite and quartz, a basic mass represented by the same minerals in association with magnetites. Accessory minerals are apatite, magnetite, zircon.

Zones of cavernous quartz and quartz-alunite alteration are traced in depth up to 400m from the day light surface (see 19.3b). It is established that in depth the thickness of alteration substantially diminishes and in depth of more than 150-200m the thickness of cavernous bodies rarely exceeds 2m. On outer parts of these tapering out bodies are formed thin margins of quartz-kaolinite composition, but alunite is recorded as sporadic. The structural interrelations of kaolinite and alunite permits to suppose that part of the kaolinite is product of replaced alunite.

Sulphid and gold mineralization in deposits are concentrated mainly in bodies of cavernous quartz. Two fundamental types of sulphid mineralization are distinguished. In depths of more than 200m develops an association of chalcopyrite+tennantite in association with pyrites and rarely encountered sphalerites. Above predominate covellite and luzonite, but pyrite, chalcopyrite, sphalerite and tennantite are rare. Gold is mineralized in the form of enclosed native gold in sulphides (mainly in pyrite). Silver mineralization on the deposit is present as electrum and admixture of covellite and stromeyerite.

R.Stoffregen [1987] has shown that silicification processes precede deposition of sulphide and gold. Sulphide mineralization forms in cavities of quartz bodies, or cements brecciated quartz. In depths of more than 200m in coalescence with sulphides there usually appears kaolinite, which is formed in exchange of alunite. Physico-chemical analysis of the parageneses performed by R.Stoffregen, has shown that deposition of ore minerals occurs in more reduced and basic surroundings, in comparison with environments of acid leaching.

Solfataric rock silicification. Solfatara appears as manifestation of hydrothermal influence of volcanoes with significant share of joint sulphur (H_2S and SO_2) in fluid phase. Condensation of steam gas mixture in solfatar channels leads to formation of acid and ultra-acid solutions. Interaction of these aggressive solutions with lateral rocks leads to formation of metasomatites in which an important place is occupied by silica minerals (opal, cristobalite, quartz), alunite, native sulphur, kaolinite. V.S.Znamensky [1990] has brought different types of metasomatic zoning on solfatar fields of Kurile volcanoes, under influence of fumaroles and paleofumaroles. A detailed description of the geological structure of influencing fumaroles in the domains of contemporary volcanism has been given by K.K.Zelenov [1972]. As an example is given a description of the solfataras of volcano Ebeko (Kurile islands).

On the slopes of this volcano (fig. 19.4) are observed outlets of thermal waters characterized by ultra-acid compositions and temperatures from 40° to 90°. The thermae come to the surface from numerous cracks in bleached rocks, opalites. At the place of exit, underlining the cracks, gets deposited colloidal sulphur. The waters in the composition are ultra-acid with a pH from 1,2 to 1,8. Amongst anions predominate sulphate-ions and chlore ($SO_4/Cl = 12$), cations are composed of basic rock-forming components: alumine, iron, alkalis.

K.K.Zelenov [1972] has shown that the correlation of cation composition of thermal waters and that of the corresponding components in unchanging andesites are identical, which testifies to the departure of cations from enclosing rocks – in sum turning into monosilicic formation. On the sketch, altering rocks form mantle-shaped covers with a common area of more than 15km², with visible thickness of 200-250m (cf. fig. 19.4). Mineral composition of altering rocks is uniform: opal, much more rarely is recorded cryptocrystalline quartz; in the form of constant admixture is present in the rocks rutile forming minute crystals. In 80% of the studied specimens is established alunite (0-10 vol.%, sometimes up to 50 vol.%). In the opalites alunite fills cavities and cracks, forms monomineral accumulation in the form of veins; in the lower part of silicified rocks are recorded barytes, zeolites, pyrites in the periphery. Chemical analyses of opalites have shown that with hydrothermal altered initial rocks Fe, Ca and Mg leach completely. Al comes out either completely or partly gets linked with sulfate-ions in alunite. Unfortunately vertical and horizontal metasomatic zoning with this occurring process of silicification has not been studied. This gap may be filled, utilizing the genetically similar examples of development of acid geotherms of Steamboat Springs.

The geothermal waters of Steamboat Springs (Nevada, USA) [White et al., 1964, Shoen et al., 1973] interact with andesites and granodiorites in the course of the period from 1 million to 100 000 years ago. In depths of 50 to 120m, at temperatures up to 170°C, on initial rocks with interaction with near-neutral (pH = 6.1) waters are formed associations of illite, quartz, chlorite, adular, albite. In near-surface conditions the outgoing geothermal waters acquire an ultra-acid character, and the initial rocks are transformed in monosilicic formations. Silicified rocks crop out on the surface in the form of mantle-shaped bodies. Owing to drilling, it was possible to study the mineral zoning of sulfatara alterations in depth (fig. 19.5). The upper part of the section is presented as opalized rocks with admixture of tridymite, alunite, kaolinite, montmorillonite, anatase. Alteration of the rocks coincides with sets of communicating cracks, filled with a mixture of opal and alunite, in those trimmings arises “bleaching” of the rocks. The earliest process is the development of montmorillonite mixing minerals of the basic mass and volcanic glass. In more altered rocks are kaolinite, mixing kaolinite and plagioclase of initial rocks. At the same stage of alteration occurs replacement of ilmenite (mineral of the matrix) by anatase. In the most transformed rocks, opalites, kaolinites and anatase are displaced by opals. The zone of opalites in depth is about 30m thick. Shoen with co-authors [1974] have established that the lower limit of opal development coincides with the level of ground waters. Lower down predominating mineral of metasomatic alteration is alunite. Alteration gives way under down to zones of development of kaolinite and montmorillonite. Pyrite usually concentrates in vacuities and cracks of altered rocks in the lower part of the opalite body and

montmorillonitized, kaolinitized and alunitized rocks. In the upper part of the opalites instead of pyrite are formed hematite and hydroxide of iron, which is linked with the passage of hypogene to hypergene regime with more oxidized conditions.

On the whole, as observes V.S.Znamensky [1990], in the alteration of mineral composition horizontally or vertically in solfatara bodies is observed a strikingly marked tendency to passage from strongly acid to feebly neutral associations. The character of mineral zoning is very much determined by the structure of the network of fissures: the presence of tubular wholly permeable zones is strikingly marked a horizontal shift of association (solfataras of the volcanoes of Baran and Chirip. Kurile islands) [Znamensky, 1989]. Analysis of the paleohydrological environment on the Maletovskoe neogene sulphur deposit (Kamchatka)

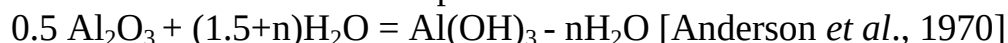
has permitted V.M.Erkine [1969] to establish that this deposit of sulphur-containing SQ is controlled by great crack structures drained by well aerated superficial waters at the time of ore-deposition. This occurs, for instance, specially in the zoning of SQ, which presents itself in symmetrical aureoles around monoquartzites, having replaced permeable layers of pyroclastic rocks. Remarkable is a regular displacement of sulphur-bearing facies of hydrothermally altered rocks from the centre of the deposit to the roof and the base. In the centre of the ore body are observed dense siliceous rocks, which in the base of the deposit give way to sulphur-bearing quartzites, but the last rocks through kaolinite-quartzitic rocks pass to montmorillonized and pyritized tuff breccias. In the roof of the deposit the zoning takes another aspect: dense monoquartzites pass into sulphuric alunite-containing quartzites, which above give way to kaolinite-quartzitic rocks, but the last varieties gradually through montmorillonite-kaolinite pass to montmorillonitized effusives displayed on the surface. In the presence of a network of small jointing in the rocks, the solfatara development is characterized by a clearly marked vertical zoning, and passage from acid associations (superficial and near-superficial parts of solfatara) to neutral ones (in depth) is observed on the vertical (Steamboat Springs).

Specific products of superficial silicifying of rocks are *siliceous sinters* in domains of contemporary geothermal systems. Siliceous sinters are widely spread in geothermal domains (Steamboat Springs, Yellowstone, Wairakei, Beovava, Pauzhetka, etc.). The study of epithermal deposits shows that their formation, as a rule, was accompanied by deposition of silica on paleo-surface in the aspect of terraces, which appear as fully analogous to the now formed sinters [Sunneen & Siltoe, 1989]. Unlike solfatara environments, formation of siliceous minerals in sinters is not accompanied with rock-leaching, but SiO_2 arises from oversaturated solutions, discharged on the surface. Therefore the sinter bodies have a hydrothermal sedimentary genesis.

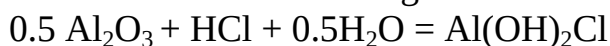
P-T parameters of S.Q formation. Experiments with the Al_2O_3 - SiO_2 - H_2O system permit to confidently enough evaluate the temperature of SQ formation. Temperature facies of SQ according to I.P.Ivanov [1993] are shown on fig. 19.6, where monovariant lines of dehydration reaction define the temperature intervals of stability typical of SQ minerals: gibbsite, kaolinite, pyrophyllite, diaspore, andalusite. The highest temperature SQ mineral is corundum. Thermodynamic calculations and experiments have shown [Zharikov, 1969, 1972; Hemley, 1980] that the corundum-quartz association is unstable (fig. 19.7). As follows from the position of monovariant lines (cf. fig. 19.6), pressure feebly influences the equilibrium determining the stability of SQ minerals. The large development of andalusite and the absence of quartzite in SQ undoubtedly testifies to the small depth of the formation of metasomatites (hypabyssal and subvolcanic facies of depth). This also corroborates the clearly marked contact character of the development of aureoles of SQ, with sharply outlined boundaries of the field of high temperature acid metasomatism deposited in lateral rocks. For a finer evaluation of pressure in SQ formation may be utilized indirect data. P.Heald [P.Heald *et al.*, 1987] with co-authors have given a report of valuation of deep formed metasomatic rocks on epithermal deposits, linked with appearance of acid leaching. Most valuations correspond to an interval of 100-500m, which, in the opinion of the authors, is determined by a pressure interval where there is boiling of a H_2O - NaCl flow. R.Stoffregen [1987] has evaluated pressure in hydrotherms on the Summitville deposit at 30 bar, at the temperature about 250°C , as a result of homogenization of an inclusion in quartz.

Mobility of alumina in SQ formation. Most experimental works on hydrothermal synthesis of minerals indicate a small solubility of alumina in aqueous near-neutral solutions.

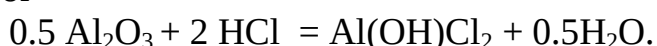
Corundum dissolves in pure water in reaction:



With increasing pressure, corundum solubility in supercritical aqueous solution grows [Becker *et al.*, 1983]. This growth forms about 7.24ppm Al_2O_3 on 1 Kb in the interval from 2.5 to 20 Kb and temperature from 670° to 700°C . K.Ragnarsdottir & J.Walter [1983] have revealed the maximum of corundum solubility at 500°C and the minimum at 600°C in the pressure interval from 1 to 3 Kb. Increase of acidity of the solution brings about a significant increase in alumina solubility. M.A.Korzhinsky [1987] has shown increase of Al solubility in salt-acid solutions in equilibrium with corundum, with the existence of the additional reaction of dissolving corundum:



and/or



Growth of alumina solubility is also experimentally established in aqueous HF solutions [Haselton *et al.*, 1988]. On fig. 19.8 is shown a combined diagram: solubility of alumina in solutions, in equilibrium with different associations and pH, constructed on data of various authors. These values have been either obtained in experiments or calculated especially for temperatures of 250-450°C. Noted are two fields of composition: 1) for solutions where acidity turns out HCl and SO₄, and 2) for solutions with HF. Chlorido-sulfatic environments are characterized by a sharp increase of Al solubility on 6 orders of magnitude with the growth of acidity. The highest values of those present on the diagram are obtained for solutions in equilibrium with Al₂SiO₃ (andalusite – cyanite) [Ostapenko *et al.*, 1987]. In contrast with alumina, silica solubility slightly grows with increasing acidity of the solutions. This fact is marked in experimental works [Haselton *et al.*, 1988, Hollands & Malinine, 1982] as well as in calculations of silica solubility in salt-acid solutions [Ivanov, 1993]. These regularities can be seen on fig. 19.9: with the growth of alumina solubility in solutions from near-neutral to ultra-acid on 6 orders of magnitude, silica solubility increases only on 0.2 orders of magnitude.

Evolution of metasomatic systems leading to SQ formation. SQ formation presents itself as an extreme degree of bleaching of metals from rocks with acid and ultra-acid solutions. As the main source of acid components in metasomatizing solutions serves a cooling magmatic melt, from which separates a fluid consisting mainly of H₂O+ CO₂+HCl+ H₂S+HF. From the preceding section it follows that bleaching processes are linked with a high activity in gradual dissociation of strong acids (HCl, H₂SO₄, HF) in aqueous solutions. Small acidities (H₂S, H₂CO₃) are lightly buffered by mineral enclosing rocks and cannot create a sufficiently acid environment indispensable for SQ formation. Correspondingly, amongst solutions producing silicification (forming SQ and products of “advanced argillization”) two groups are distinguished: a chloridic, with which is linked a substantial SQ, and a sulfate, producing argillization.

In the process of cooling of magma and of a flow separating from it, HCl is redistributed in the flow. The contemporary state of the question of HCl behaviour in magmacrystallization is minutely examined in the work of [Malinine & Kravchuk, 1995]. It may be cited as established that with pressure of less than 1Kbar concentration of chlorides in fluid phase grows with time until complete crystallization of magma. A reverse picture is observed at a pressure of more than 1 Kbar. The higher the initial water content in the melt, the higher the speed of decrease of chlore content in the separating flow. If we admit that chlore concentration in acid melts reaches 3000g/t and the coefficient of distribution $K_{cl} = X_{fl} / X_{melt} = 30$, chlorine concentration in cooling magmatic fluid solution may reach the value 0.09 g/l (or 2.5m).

Oxygenous combinations of sulphur also play an important role in SQ formation. S.N.Gavrikova [1971], on the example of Central Kazakhstan, was one of the first to draw attention to the fact that variations of the temperature and H_2O/H_2SO_4 ratio in solution determine SQ parageneses and the character of ore loading. Formation of sulphuric acidity may occur by several means [Rye *et al.*, 1992]: 1) by oxidation of sulphides in hypogene conditions; 2) by oxidation of atmospheric oxygen in horizontal ground waters H_2S , acting from deep boiling hydrothermal systems; 3) by means of disproportional magmatic SO_2 on H_2S and H_2SO_4 , with concentration of the magmatic flow on intermediate depths of hydrothermal systems. The first of the proposed mechanisms is determined by formation of zones of hydrogen oxidation (for example, at solfataras argillization); a second type is realized in epithermal deposits of adular-sericitic type ("low sulfidation") [Hedenquist, 1992]. A third mechanism, in which one of the basic factors is an increase of oxygen activity in motherly magmas, leading to a type of acid sulfidation ("high sulfidation") of epithermal and porphyritic deposits. The SO_2/H_2S ratio in the magmatic flows is a function f_{O_2} , determined by the reaction:



This dependence is shown on fig. 19.10, illustrating the alteration of volatile SO_2 and H_2S in the flow as function f_{O_2} for a magmatic flow existing in equilibrium with a magnetite-pyrrhotite association (solid solution) ($P=0.5Kb$, $T=727^\circ C$).

Concentration of magmatic flow at decreasing temperature leads to disappearance of SO_2 . H.Holland [1965] and later J.Whitney [1988] have considered alternative reactions, determined by transformation of magmatic sulphur (mainly SO_2):



and



Thus, the H_2O/H_2 ratio in magmatic fluid will determine a corresponding deposition of reactions 1 and 2 in transformed SO_2 at cooling. Starting from this, J.Whitney [1988] has shown that the sulfate type of metasomatism is very much determined by an oxidizing – reduction condition in the motherly magmas. Namely, the evolution of the flow of oxidized magmas by disproportioned SO_2 leads to metasomatism with high activity of sulfate sulphur.

An additional mechanism, special to the appearance of hydrothermal solutions in high H_2SO_4 , HSO_4^- , SO_4^{2-} concentration is boiling in hydrothermal reservoirs. The m^v/m ratio (m^v , m is the molarity of volatile in steam and liquid phase respectively) at a temperature of $350-200^\circ C$ for H_2S is 2-5 times greater than for SO_2 [Drummond & Ohmoto, 1985]. Therefore boiling of solutions must

lead to enrichment of the liquid phase of SO_2 and unification of slightly volatile components, H_2 , H_2S (fig. 19.11).

Isotope research. Isotope researches, immediately touching metasomatites forming bodies of SQ are relatively few. As most interested in fine grain of actual material and method of investigation may be cited the work of R. Rye [Rye *et al.*, 1992] in which for establishing the genesis of solutions is utilized the isotope composition of alunite. The informative value of such an approach is conditioned by the fact that this mineral can take four positions in which may be distinguished variations of stable isotopes: H/D , $\delta^{18}\text{O}$ (in position OH), $\delta^{18}\text{O}$ (in position SO_4), $\delta^{34}\text{S}/^{32}\text{S}$. As a result of such research it was shown that silicification processes in the epithermal deposits of Summitville are linked with a disproportional magmatic SO_2 and the formation of ultra-acid solutions. In contrast to that, alteration of the outer shell of metasomatic bodies of quartz-kaolinitic composition is linked with combined solutions of magmatic-meteoric origin. Research on isotope composition of alunite on the contemporary hydrothermal systems of Steamboat Springs, Waiotapu, have shown that processes of ultra-acid leaching are linked with H_2S oxidation of meteoric waters at the level of ground waters.

Isotopes of oxygen has been studied on solfatara appearances of the province San Juan [Larson & Taylor, 1987]; one appearance in this province is the epithermal Summitville deposit, characterized above in detail. It is established that variation of isotope composition of oxygen of metasomatite (chiefly quartz) is closely correlated with depth, which in the opinion of the authors, testifies to predominating control of isotope composition of oxygen by processes of boiling of hydrothermal flows (fig. 19.20). Interesting are the results of comparative analysis of isotope oxygen on solfatara appearances in this province. Amongst the studied occurrences highest $\delta^{18}\text{O}$ values in metasomatic quartz are observed on the occurrences accompanied with mineralization. Moreover, a maximal height of $\delta^{18}\text{O}$ is observed on the Summitville deposit, the richest ore object of the province, which may be linked with an increased share of magmatic flow in the source of hydrothermal solutions on ore-bearing manifestations [Larsson & Taylor, 1987]. Thus, independent results of isotope research on alunite and quartz, with use of different methods, lead to an unambiguous conclusion about the participation of magmatic fluids in the formation of metasomatic SQ zones.

Detailed isotope studies have been carried out [Klein & Criss, 1988] on paleohydrothermal systems of Precambrian early Paleozoic age of the Carolina State belt (USA) [Schmidt, 1985]. The example is interesting in that an erosion section of metasomatites represented on outcrops overturns on the side after the formation of this hydrothermal system has been completed. A schematic geological map of one of the zones of Pilot Mountain is offered on fig. 19.13. The region is mainly situated in middle-acid volcanates intersecting stocks of

dacitic porphyries, and quartzic monzonites. Zones of metasomatic alteration spatially gravitate to the stocks of dacitic porphyries. Metasomatic changes are distinctly zonal. Background alterations are weak sericitization and pyritization. An interesting metasomatism has been produced on an area of 4x2 km and presents intense rock silicification, development of lenticular bodies of quartz-pyrophyllite, quartz-andalusite-pyrophyllite composition and massive bodies of pyrophyllite composition. The general expansion has intersecting veins of quartz-pyrophyllite composition ($\pm$ sericite, $\pm$ kaolinite). The central part of the metasomatic body is characterized by intense crushing of silicified rocks, development of a quartz-topaz association. With development of metasomatites are spatially connected geochemical Cu, Mo, Sn, Au, B anomalies. The authors of the cited works have closely studied the variations of $\delta^{18}\text{O}/^{16}\text{O}$ in mineral metasomatites. Calculated temperatures of isotopic quartz- H_2O equilibrium characterize the interval of $300\pm 50^\circ\text{C}$, and at the same time isotopic equilibrium between pyrophyllite and quartz is broken (some authors compare this with the subsequent metamorphic history of the region). Calculated isotopic oxygen-hydrogen of flow mark come across the line of isotope composition of meteoric waters. An interesting detail in the development of SQ is the distribution of the $\delta^{18}\text{O}$ value in space. A relatively back stage value is that the field of development of silicification is comparatively clearly distributed at increasing values of $\delta^{18}\text{O}$ (5-6‰), whereas the stock of dacite porphyries is characterized by minimal values of $\delta^{18}\text{O}$ (< 2‰). So, in a small part of the development of metasomatites the zones are linked with highest and lowest $\delta^{18}\text{O}$ values.

Most data on isotope sulphur characterize copper-molybdenite-porphyric hydrothermal systems, which are discussed at length in a series of research works. The chief peculiarity of isotopic composition of sulphur, sulfides and sulfates is a narrow range of ^{34}S , from -3 to +1 and from +8 to 15‰ respectively. As an example of such values is characteristic an isotope composition of sulphur on epithermal deposits [Heald *et al.*, 1987], which may indicate a predominantly magmatic origin of the sulphur.

So, formation of SQ is linked with metasomatic influences of ultra-acid solutions of polygene genesis. In rear zones of transformation, where acidity of the solutions is maximal, arises a full dissolving of minerals, except quartz. As a result of interaction with the rocks, acidity of the solution decreases, to which testifies the exchange of monoquartzic with quartz-clayed or quartz-sericitic composition of zones. Therefore must occur a sharp diminution of equilibrated concentration of alumina in the solutions and an intense deposition of high aluminous minerals such as andalusite, corundum etc. Such alterations of alumina solubility contrasts with the behaviour of silica solubility, for which such a jump of solubility is not observed. Consequently, filtration and interreaction of ultra-acid solutions with rocks must lead to formation of

monoquartz bodies in kernel parts (where arises dissolving of all rock forming minerals) and a high alumina halo around these bodies.

Similar zoning and succession of mineral formation with change of solubility of the metals and their deposition reflects the passage of a wave front of acid components, detected and studied by D.S.Korzhinsky [1955]. In conformity to this model, components depositing in various acidophily behave differently in acid metasomatism. Amphoterites (alumina) dissolve, but do not experience a significant displacement in space. After the passage of the acid front they deposit here, in rocks and cracks in the quartz. Alkalis and alkaline earths are not related with the solution and may either precipitate on limits of silicified rocks or scatter in subterranean waters. The most effective processes of formation of ultra-acid solutions occur at boiling and disproportional magmatic fluid. Namely in this process are attained the highest concentrations of sulphuric acid, which provides for the high solubility of such solutions. Peripheral parts (in horizontal as well as vertical direction) present alkaline metasomatites (advanced argillization) formed by mixing of ultra-acid magmatic fluids with meteoric waters.

Ore mineralization in S.Q. High aluminous corundic SQ develop as raw materials for obtaining aluminium, but basically for obtaining technical corundum (abrasive). Rocks of the SQ type are studied in molybdenite – porphyric deposits, situated in contact zones of huge massifs of granite-porphyrries. In the Climax deposit molybdenite forms networks of veins and accumulation in quartzites, associating with sericite, but, in deep horizons, with orthoclase. In connection with more basic magmas of granodiorite-porphyry silicification occurs more seldom, and the chief type of exchange of rocks occurs with sericitization. In sericitized rocks stockwerk appears made up of veinlets of chalcopyrite and molybdenite, associated with quartz and sericite. Other spatial correlations are observed between silicified rocks and pyrite ores. Zones of silicification and quartz-sericite rocks dispose themselves under a deposit of massive sulfides in the domain of the channel on which have entered ore solutions. Habitually the composition of these zones are of quartz+pyrite or quartz+sericite+pyrite, but in comparatively rare cases have been described quartzites with corundum, andalusite and diaspore, accommodated in the same position.

The situation is more complex with silicified rocks in intervals of gold-silver deposits. There usually appear facies of hydrothermal argillitized rocks, which also appear as ore-containing. Silicified solutions (monoquartzites, quartz-kaolinite, quartz-alunite rocks) often compose a field of deposited lenses or layer-formed bodies, which serve as screen for ore-bearing solutions in a sericite-adular type of deposit. In the acid-sulfatic type of deposit silicified rocks with diaspore, andalusite, sometimes with alunite are encountered immediately in ore veins of steeply dipping metasomatic zones.

In volcanic domains are spread opalites and near-surface quartzites, contained as deposit fossil native sulphur, which forms veins, lenses and disseminated accumulation in quartz or in opal. Vertical zoning is observed, consisting of sulphur opalites in succession from below upwards with massive sulphides of iron (Matsuo deposit in Japan, on volcan Mendeleev on Kunashi island). Sulphur quartzites contain gold pigment and set down tubular bodies, traced on Paramushir island on a depth up to 300m.

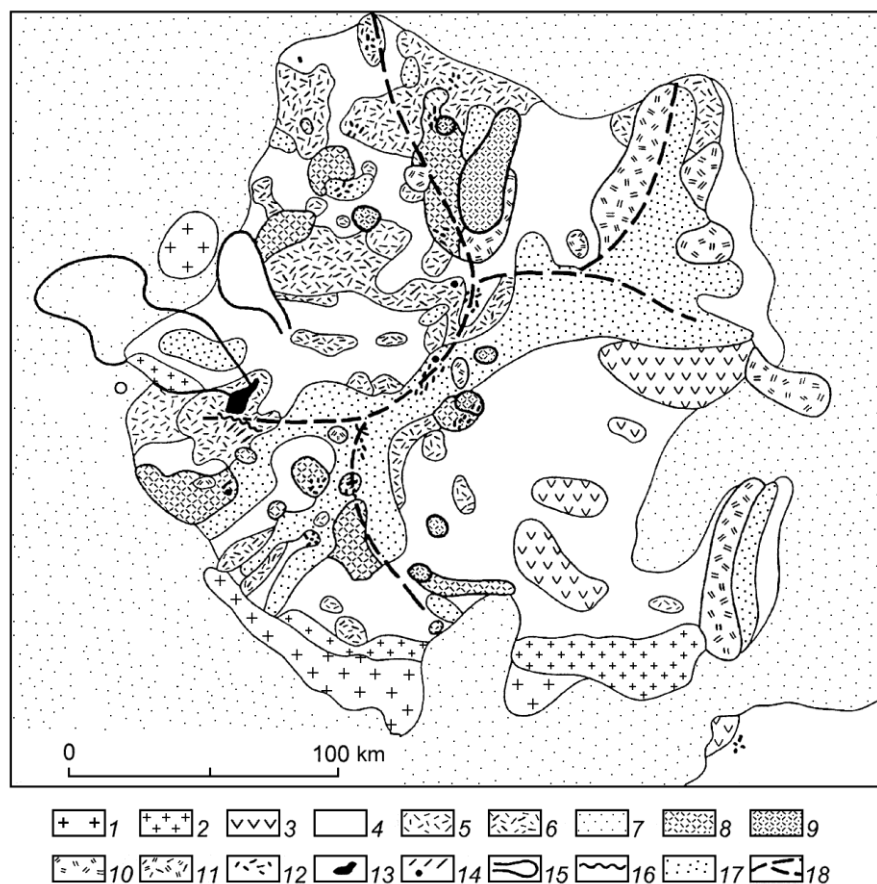


Figure 19.1. Geological outline of alunite-andalusite-corundum deposit of Semiz-Bugu [Nakovnik, 1964].

1– granites; 2–granite-porphyrries; 3–acid affusives; 4–sericitic secondary quartzites (SQ); 5–quartz-sericitic rocks; 6–quartz-sericite-andalusitic rocks; 7 – monoquartzites; 8, 9 – andalusitic SQ; 10–alunitic SQ; 11–alunite-andalusitic SQ; 12–area of development of veinlets and dissemination of corundum; 13–main corundum body; 14–small corundum bodies; 15–detritic corundum; 16–dykes of diabbases; 17–alluvium; 18–axial lines of ridges.

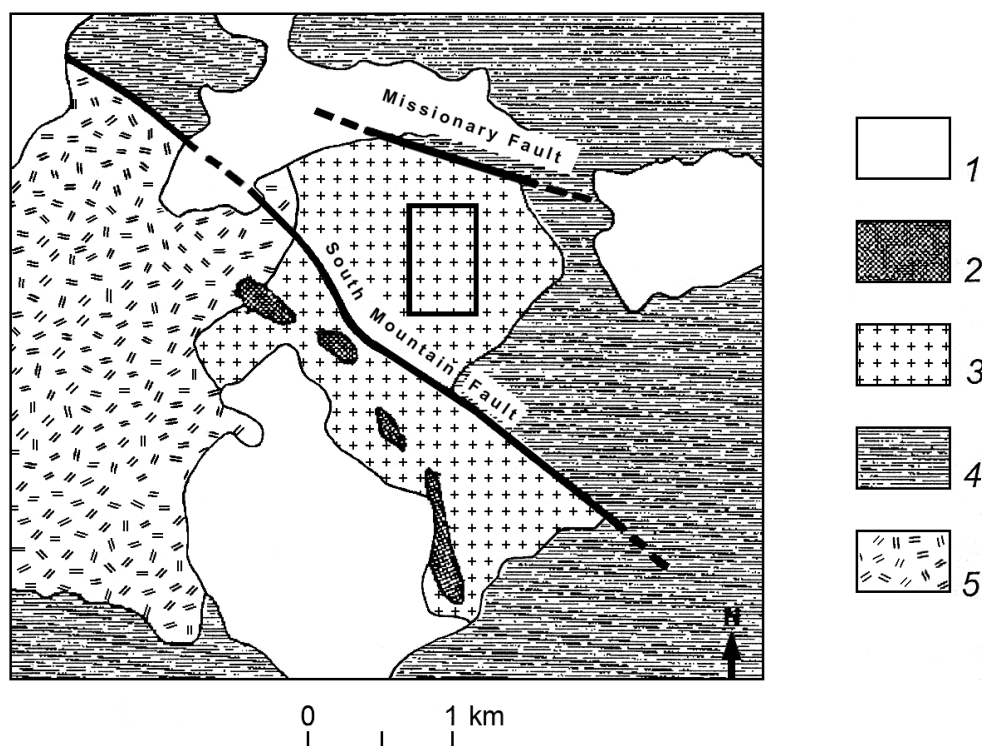


Fig. 19.2. Geological map of district of Summitville deposit [Stoffregen, 1987].

1– quaternary; 2–rhyolites (18-20 million years); 3–quartzic latites (21-23 million years); 4–andesites (26,6 million years); 5–rhyodacites (27,7 million years); quadrangle surrounds limits of area on fig. 19.3a.

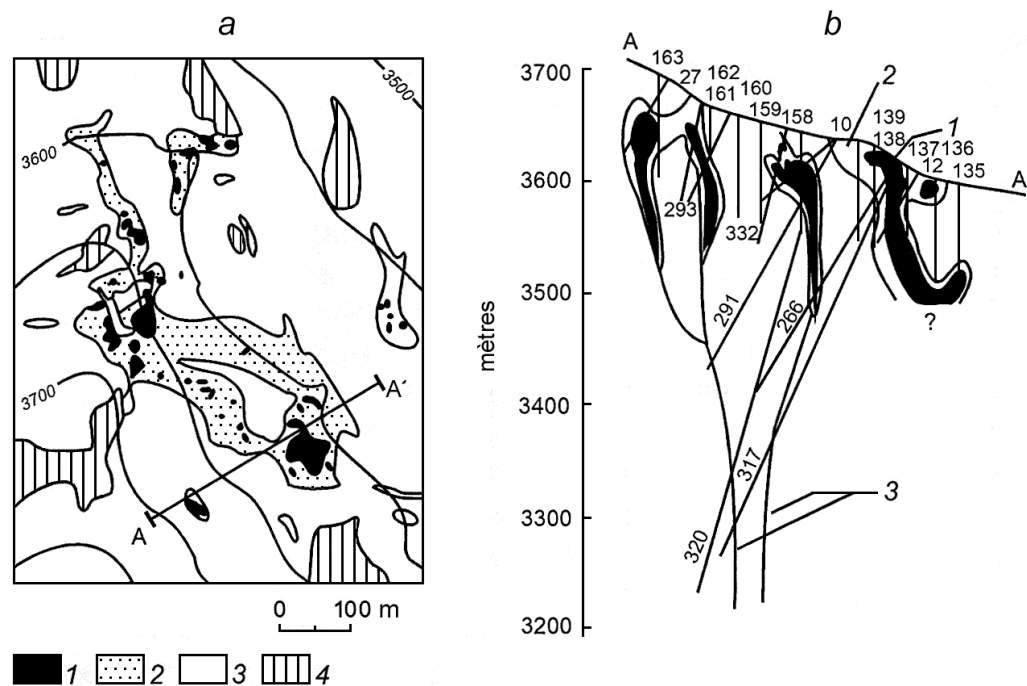


Fig. 19.3. Distribution of basic types of altered rocks on Summitville deposit [Stoffregen, 1987].

a – areal distribution: 1 – bodies of cavernous quartz; 2 – undifferentiated quartz-alunite-kaolinite alterations; 3 – acid alterations; 4 – fresh rocks; *b* – cross-section in A-A profile. Distribution of bodies of cavernous quartz (1) and quartz-alunite alterations (2) on vertical with depth transition into slightly thick (1-2 m) bodies of cavernous quartz (3) with quartz-kaolinite margin.

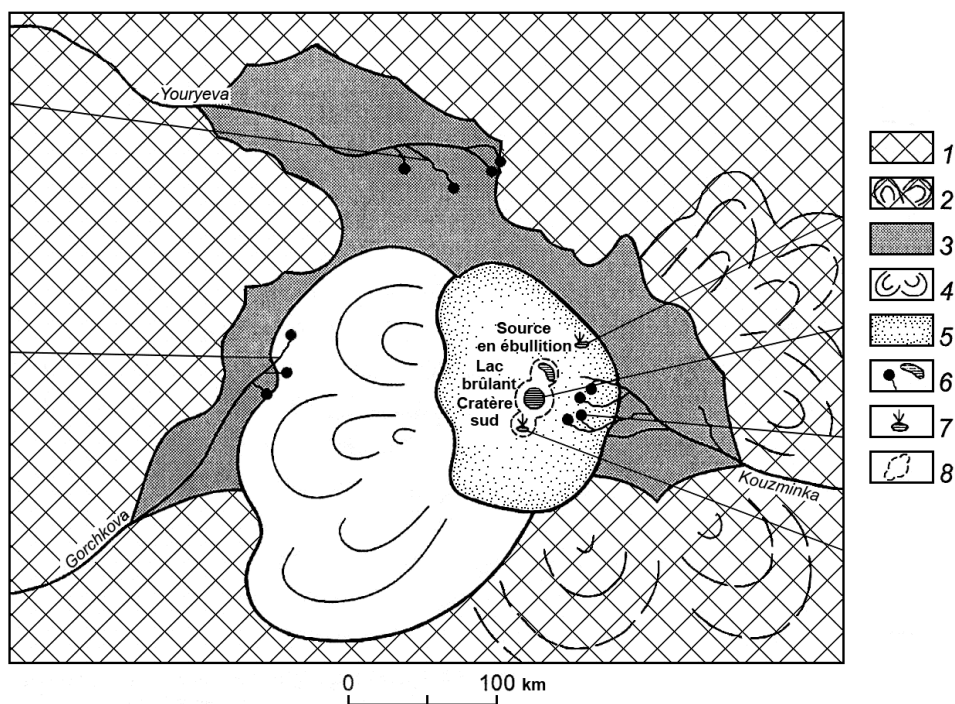


Fig. 19.4. Geological map of Ebeko volcano [Zelenov. 1972].

1—fresh basic lavas and tufas; 2—old volcanic cavernity; 3—zones of opalite development; 4—young andesites; 5—pyroclastic rocks; 6—acid source and lake; 7—solfatara; 8—craters of volcano. White spring Hotter lake South crater

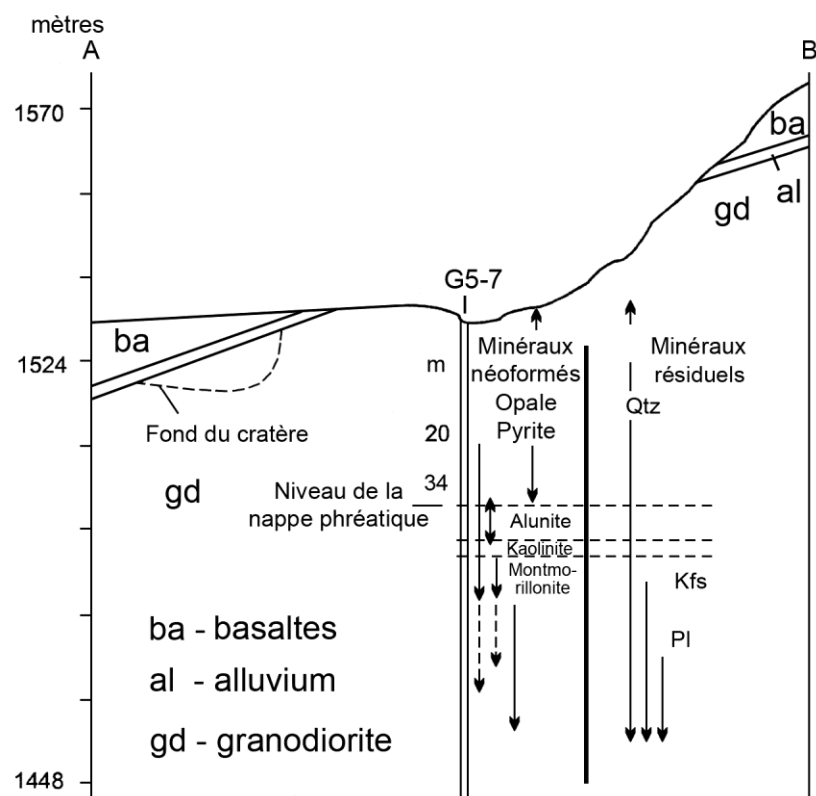


Fig. 19.5. Distribution of newly formed minerals in a vertical cross-section of the Steamboat-Springs deposit [Schoen et al., 1974].

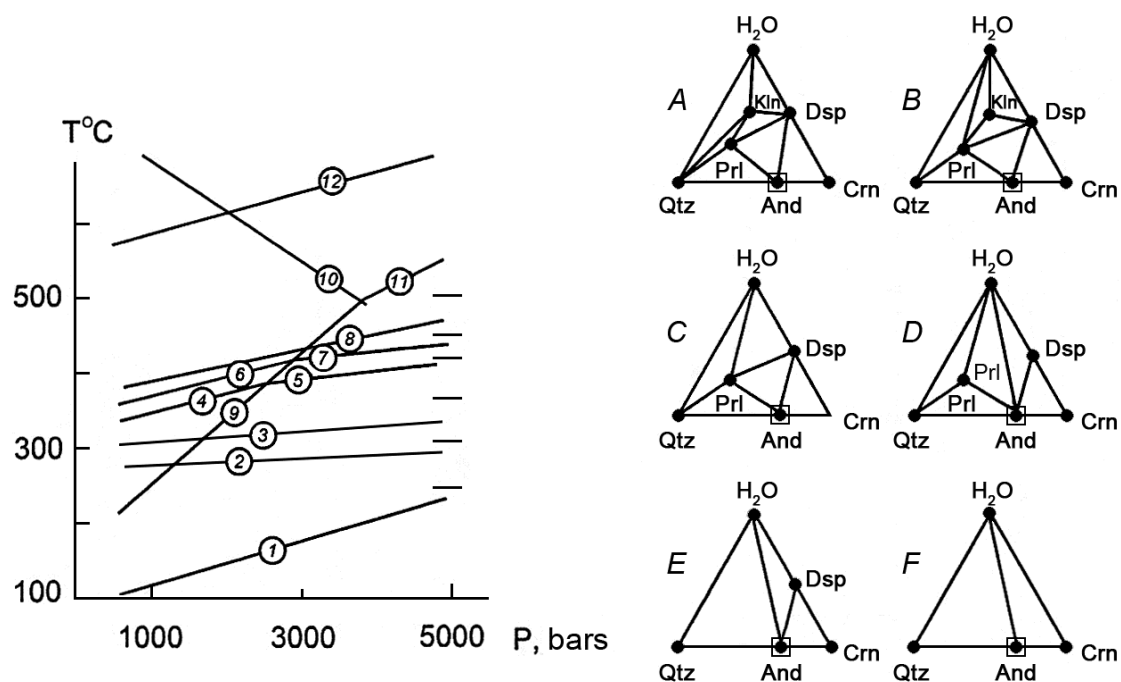


Fig. 19.6. T-P diagram of the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ [Ivanov, 1993]

Univariant reactions: 1. $\text{Gib} = \text{Dsp} + \text{H}_2\text{O}$, 2. $2\text{Qtz} + \text{Kln} = \text{Prl} + \text{H}_2\text{O}$, 3. $2\text{Kl} = \text{Prl} + 2\text{Dsp} + 2\text{H}_2\text{O}$, 4. $\text{Prl} + 6\text{Dsp} = 4\text{And} + 4\text{H}_2\text{O}$, 5. $\text{Prl} + 6\text{Dsp} = 4\text{Ky} + 4\text{H}_2\text{O}$, 6. $\text{Prl} = 3\text{Qtz} + \text{And} + \text{H}_2\text{O}$, 7. $\text{Prl} = 3\text{Qtz} + \text{Ky} + \text{H}_2\text{O}$, 8. $2\text{Dsp} = \text{Cor} + \text{H}_2\text{O}$, 9. $\text{And} = \text{Sil}$, 11. $\text{Sil} = \text{Ky}$, 12. $\alpha\text{Qtz} = \beta\text{Qtz}$. A-F parageneses of facies on triangular composition-paragenesis.

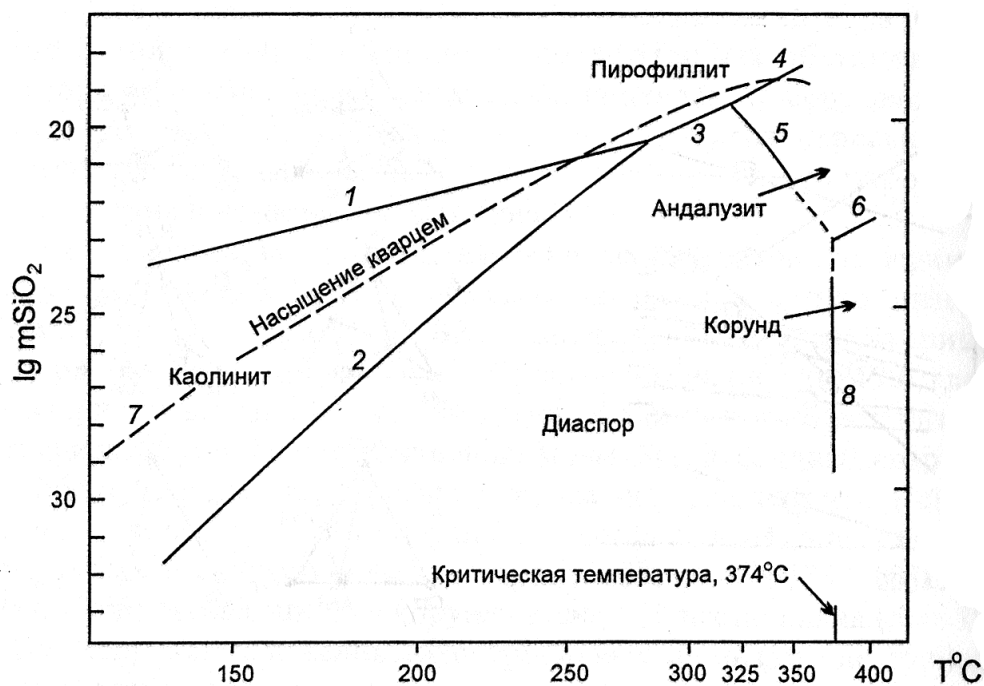


Fig. 19.7. Stability fields of minerals on diagram T-log m_{SiO_2} in Al_2O_3 - SiO_2 - H_2O system along curve of boiling of water [Hemley et al., 1980].

Notation for reactions: 1. $\text{Prl} + 5\text{H}_2\text{O} = \text{Kln} + 2\text{H}_2\text{SiO}_4$, 2. $\text{Kln} + 3\text{H}_2\text{O} = 2\text{Dsp} + 2\text{H}_4\text{SiO}_4$, 3. $\text{Prl} + 8\text{H}_2\text{O} = 2\text{Dsp} + 4\text{H}_4\text{SiO}_4$, 4. $\text{Prl} + 5\text{H}_2\text{O} = \text{And} + 3\text{H}_4\text{SiO}_4$, 5. $\text{And} + 3\text{H}_2\text{O} = 2\text{Dsp} + \text{H}_4\text{SiO}_4$, 6. $\text{And} + 2\text{H}_2\text{O} = \text{Crm} + \text{H}_4\text{SiO}_4$, 7. $\text{Qtz} + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$, 8. $\text{Crm} + 3\text{H}_2\text{O} = 2\text{Dsp}$.

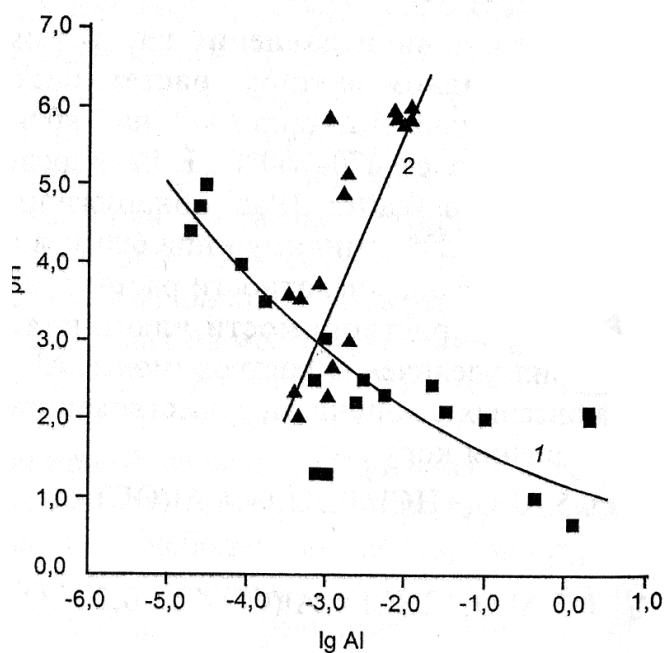


Fig. 19.8. Dependence of solubility of aluminium (mol/kg) upon acidity of saline and sulfate solutions (quadrants and curve 1) and fluorid solutions (triangles and curve 2) in temperature interval 250-450°C.

Constructed on data of experiences and thermodynamic modeling [Becker et al., 1983; Stoffregen, 1987; Korzhinsky, 1987; Ostapenko et al., 1987; Haselton et al., 1988; Ivanov, 1993].

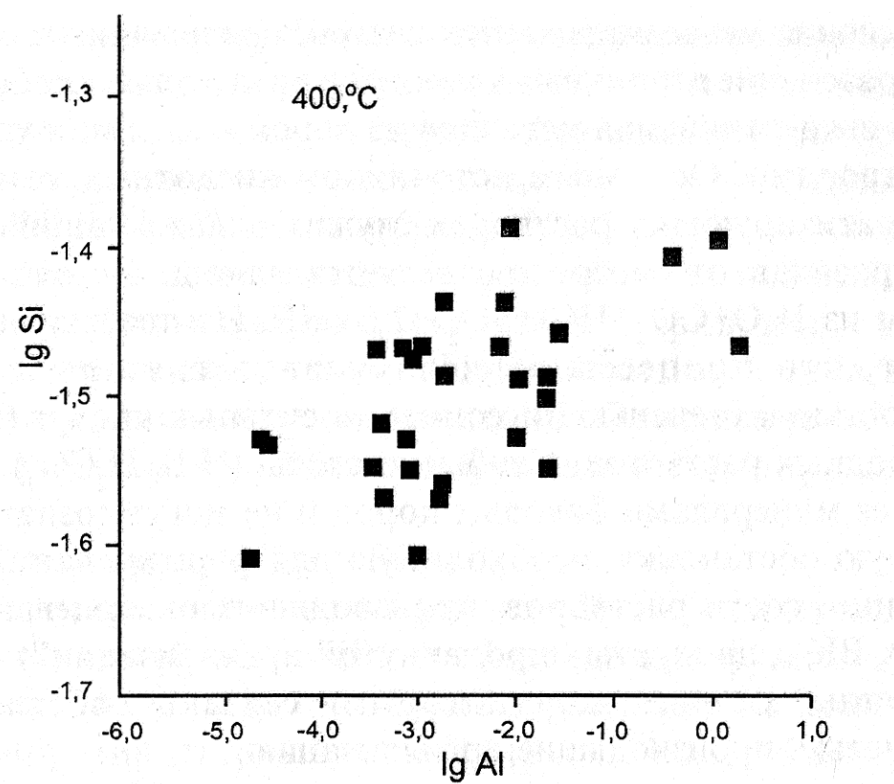


Fig. 19.9. Correlations of solubility of silica, solubility of aluminium (mol/kg) in muriatic and fluorid solutions at 400°C after data of [Haselton et al., 1988; Ivanov, 1993].

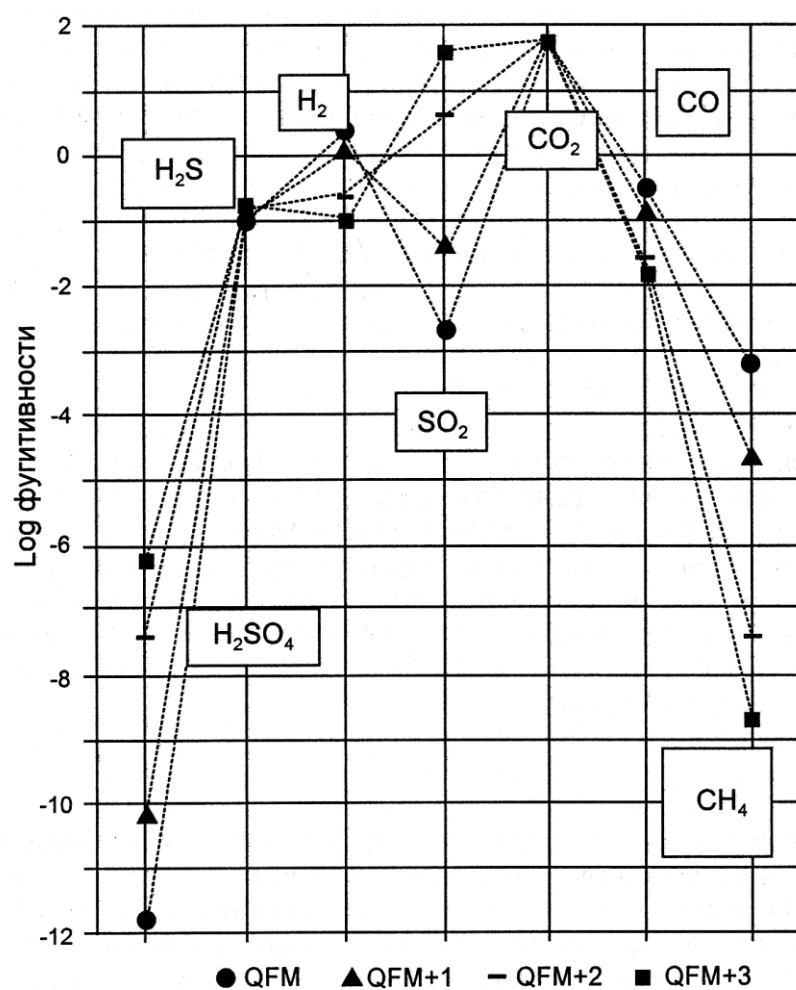


Fig. 19.10 Volatility of basic components of a magmatic fluid in equilibrium with magnetite and pyrrhotite at f_{O_2} equal QFM, QFM+1, QFM+2, QFM+3 and 727°C, 500 bar, $X_c=0.1$.

Values f_{S_2} and f_{O_2} are given for equilibrium of pyrrhotite (solid solution)-magnetite after data of [Whitney, 1984]. The parameter X_c equals the sum of mole parts of CO₂, CO, CH₄ in the fluid.

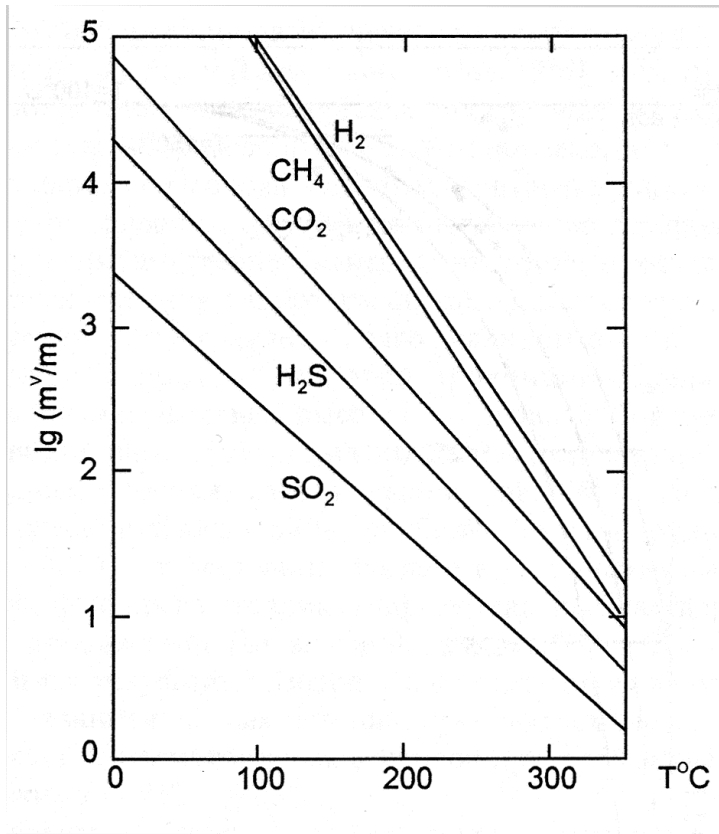


Fig. 19.11. Temperature dependence of parameter $\lg(m^v/m)$ for basic components of an aqueous hydrothermal fluid [Drummond and Ohmoto, 1985].

m^v and m , molar concentrations of gases in steam and liquid phase respectively.

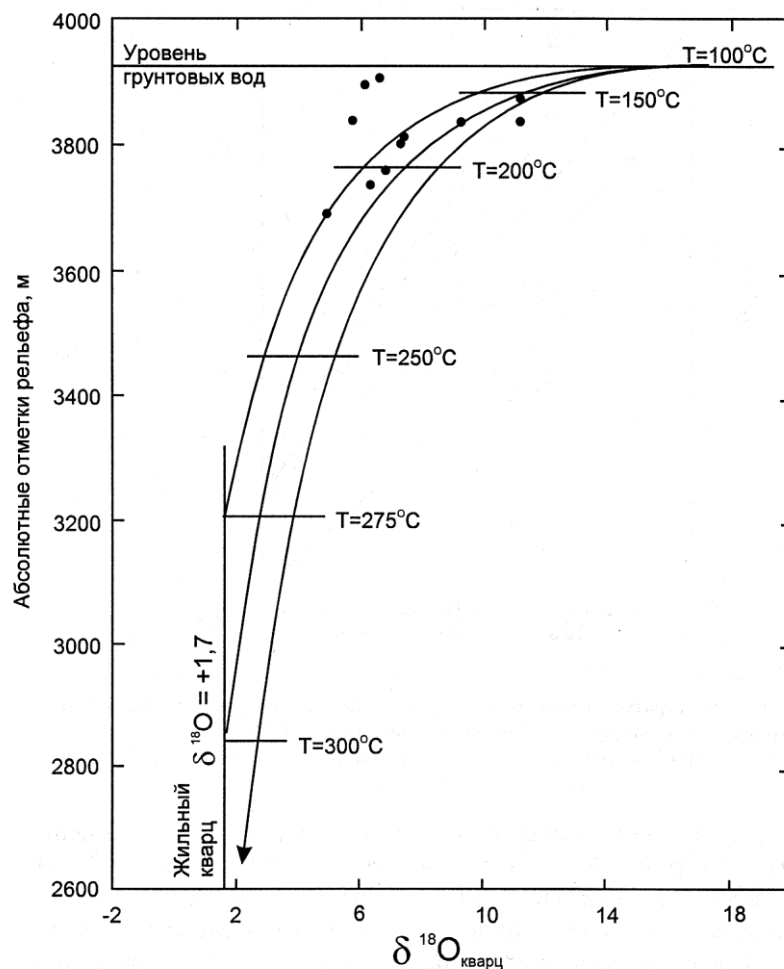


Fig. 19.12. Calculated model of isotopic composition variations ($\delta^{18}\text{O}$) of hydrothermal quartz in equilibrium with an acid fluid with initial boiling temperature of 275, 300, 325 $^\circ\text{C}$ for solfatara manifestation in the San Juan province [Larson & Taylor, 1987].

Points indicate dimensions of $\delta^{18}\text{O}$ value in hydrothermal quartz in vertical cross-section of a hydrothermal system.

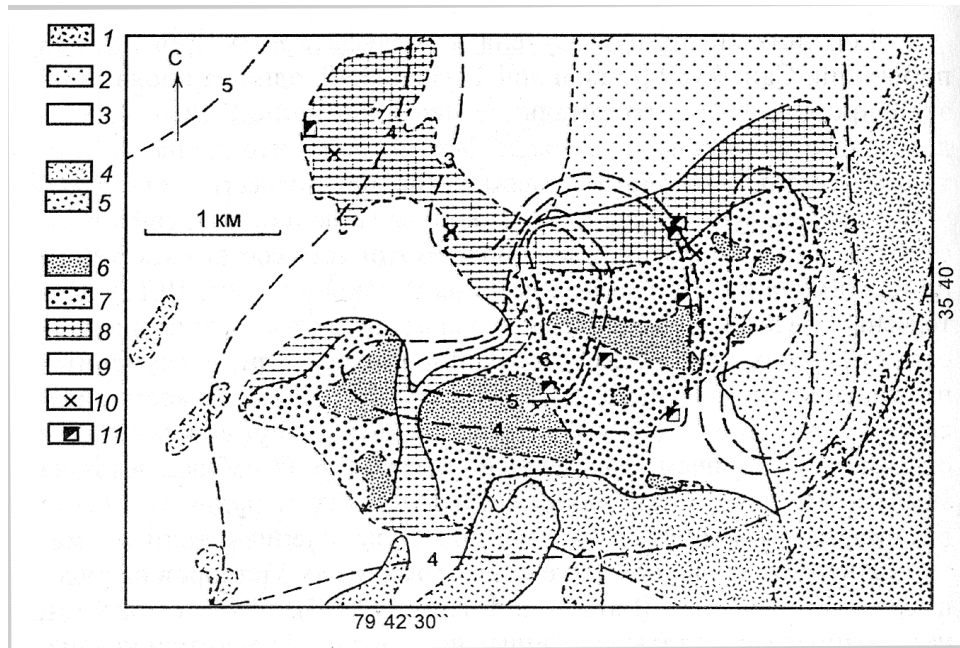


Fig. 19.13. Geological map of ore area of Pilot Mountain [Klein & Criss, 1988].

1–acid volcanic rocks; 2–arenites, clays; 3–andesites; 4–quartz monzonites; 5–dacite porphyries, altering rocks; 6–Qtz-Prl-And; 7–Qtz; 8– Chl-Ser; 9 –Qtz-Ser; 10 –points of gold ore mineralization; 11– abandonment of gold ore reefs. Dotted lines indicate isolines of $\delta^{18}\text{O}$ in the rocks.

CHAPTER 20

Beresites and beresitized rocks

Definitions. The term “beresites” in its original sense designates metasomatically altered granites near quartz-gold ore veins, composed of sericite, quartz, pyrite and ankerite. Beresites are formed as a result of acid metasomatism with high carbon dioxide fugacity. Subsequently similar ones have been investigated in the composition of rocks transformed not only at the expense of granites but also on other intrusives, volcanic and volcanogene-sedimentary rocks in an analogous process of acid metasomatism. The term “beresite” is applied to metasomatic rocks of quartz+sericite + ankerite + pyrite composition, i.e. to rocks of inner zones of metasomatic columns. To moderately or feebly altered rocks of outer zones of transformation is applied the term “beresitized rocks”. Such an interpretation of so-called ore-enclosing rocks was already put forward by N.I.Borodaevsky and M.B. Borodaevskaia [1947], and the process of their formations was called beresitation. The mineral composition of beresitized rocks varies: apart from ankerite, may be present other carbonates, and principally are encountered quartz-sericitic (non-carbonatic) varieties, etc.

Beresitation presents itself as one of the most widely spread types of near-vein transformation and was seen in connection with deposits of gold, silver, polymetals, uranium, fluorite, molybdenum. Beresites have long since attracted the attention of researchers, which can be seen in the abundance of works devoted to this type of transformation. The term “beresite” was proposed by G.Rose in the middle of the nineteenth century for sericitized granite-porphyrries and aplites of the gold ore Berezov deposit in the Ural. Later these metasomatic formations were studied in detail by A.P.Karpinsky, V.V.Nikitine, A.N.Zavaritsky, N.I.Borodaevsky, M.B.Borodaevskaia, D.S.Korzhinsky and many others. Thanks to D.S.Korzhinsky’s ideas in the succeeding time progress was made in the study of the genesis of this type of transformation which was

specially accompanied by the works of G.P.Zaraisky, U.B. Shapovalov, B.I.Omelyanenko, V.A. Zharikov, devoted to theoretical and experimental modeling of beresitation processes. These processes, forming on rocks of ultrabasic composition, have received the name of listwaenitization owing to the green colouring of arising metasomatites. They have a quartz-carbonate, talc-carbonate and fuchsite-quartz-carbonate composition. "Beresitation" is a notion used only in Russia. In foreign literature, a synonym is "sericitization", but if the term beresite is utilized, it is only concerning the gold-ore deposits of Russia and with reference to Russian researchers.

Parageneses of quartz with sericite and carbonates are of themselves yet no indicator of metasomatic family of beresites, insofar as it can also be observed in rocks of another genesis, for instance in sediments having undergone initial metamorphism. In complex cases it is necessary to employ a combination of signs, the principal of which are geological setting, structure control, mineral composition, character of metasomatic zoning and presence of ore mineralization. Non-carbonatic facies of beresites arise in acid magmatic rocks (aplites, leucogranites), impoverished in calcium and magnesium. Quartz-sericitic metasomatites sometimes precede in a special formation, characteristic, grosso modo, of pyrite and pyrito-polymetallic deposits [Zharikov and Omelianenko, 1965]. Quartz-sericitic near-ore rocks are characteristic also of deposits of copper and molybdenum of porphyric type, in which they closely associate with SQ.

Geological position of beresite formation. Beresite extension is limited to domains of development of an orogene granitoid magmatism in a crust of continental type. The time interval of their development is from late Precambrian to Mesozoic-Cenozoic, but the maximal extension of beresites occurs in the Hercynian and Mesozoic epochs. The process of beresitization occurs after full completion of intrusive and effusive magmatism, and they are preceded by the appearance of metasomatism at the magmatic stage. Intersections of beresites with magmatic bodies are possible if the latter belong to a later magmatic cycle. In the evolution of the hydrothermal process, after beresitization occurs ore mineralization and may develop low temperature argillization.

Beresitized rocks present themselves as typical peri-ore metasomatites on many middle-deep (2-3 km) deposits in Paleozoic domains (Ural, Kazakhstan, Central Asia, Central Europe, Appalachians, Eastern Australia), and also Mesozoic deposits (Transbaikalian region, Mongolia) of orogenesis and tectonomagmatic activation. In domains of Quaternary and contemporary volcanism typical appearances of beresitization are unknown.

Areas of extension of these metasomatites wholly coincide with the domains of development of granitoid intrusive massive subvolcanic bodies or regional dyke belts, characteristic of ore-districts of the Transbaikalian, Central

Asia, etc. A genetic link of beresites with magmatism was established on the example of the Kurama volcano-plutonic belt in Central Asia [Abramov *et al.*, 1995].

Beresites belong to metasomatites of local extension. They are distinctly controlled by fracture zones or thick zones of lamination and cataclasm. In the latter case the total thickness of beresitization aureoles attains many hundreds of metres. Thus, the predominating form of metasomatic bodies is near to veinous or stratiform but the thickness of this strata reaches 100 and more metres in effusive and sedimentary rocks. The problem of the family-belonging of such so-called back-ground regional zones of sericitization in volcanic masses remains until now under discussion, and the criteria of development zones of regional quartz-sericitic transformation and near fracture beresites are undefined. A direct link between them may also not exist and the geologico-structural conditions of their appearance may be strongly different. So, strictly beresites or “full-appearing metasomatites”, according to E.V.Plushev [1981] superficially distinct gravitate around fractures and are linked with hydrothermal flows, whereas slightly changed beresitized rocks may attain thickness of tens of km², not displaying however a distinct confinement to cracks and fissures and an obvious link with magmatism.

Beresites precede ore-deposition occupying a volume of rocks, significantly exceeding the volume of the ore bodies. Veinous metasomatites associates to ores or periveinous metasomatites (chloritic, carbonatic, albitic, etc) are spread only in inner zones of beresitization columns.

Mineral composition. To the number of chief minerals occurring in the composition of beresite family are quartz, sericite, carbonates, chlorite, pyrite, fuchsite.

Sericite is the chief typomorphic mineral of beresites. Crystallo-chemical and structural peculiarities of sericites are uniform, independent from the facies. The problems of nomenclature of dispersed potassium mica have been partially treated in a work devoted to this group of minerals [Omelianenko *et al.*, 1982]. To sericites it is proposed to relate fine scale micas, varying in composition between muscovite, phengite and illite; moreover isomorphism of the muscovite-phengitic type is predominant in the strictly beresites, but isomorphism of the illitic type predominates in their lower temperature facies. Content of swelling interstices of the smectitic type in sericites may not exceed 5%, that of hydromicas 15%, but in mixed-layered minerals of micasmectitic type it varies from 15 to 45%. These definitions of sericites and hydromicas are not universal, and in foreign literature to sericites are related all fine-scaled potassic bright micas of hydrothermal genesis, containing up to 40-50% interstices of the smectitic type. Fine-scaled micas of beresites answer to polytypical modification 2M₁, or a mixture of 2M₁+1M with predominance of the first, the polytype 3T much rarer.

Chemical composition of sericites differs from theoretical muscovite by increased content of silicon and decreased content of aluminium (fig. 20.1). Near the muscovites are micas from gold-bearing hypabyssal beresites. Degree of mica phengiticity may change in the limits of one deposit, changing in the direction of the ore vein. Micas from low temperature facies of beresitized rocks have illitic composition (formula of illite $K_{0,75}(Al_{1,75}R^{+}_{0,25})Si_{3,5}Al_{0,5}O_{10}(OH)_2$). It can be seen on the diagram that mica compositions from typical beresites are approximately embedded on the line of muscovite-phengite. Distinctly distinguished from them are the dispersed micas from lower temperature hydromicaceous metasomatites. These differences are also well surveyed in other diagrams (fig.20.2). Sodium micas (paragonites) are relatively rare in beresitized rocks, they are more often encountered in listvenitized basic rocks. Examples are known of development in perire metasomatites of a mixture of paragonite and muscovite or combined minerals of the muscovite-paragonitic type, which are counted as result of imposition on metasomatic processes of regional metamorphism. However, research by A.I.Grabezhev [Grabezhev *et al.*, 1945] of gold ore deposits of the Ural have revealed the regular presence there of paragonites and beresites. It is possible that this mineral was not replaced earlier because of its similarity with potassic micas.

Anion composition of sericites has on the whole no clearly marked specific character. In some gold-silver-polymetallic epithermal deposits, but also in uranium deposits in volcanic masses, sericite contains a noticeable quantity of fluor, up to 1 mas.%. This is comparable with the fluorine content in micas from higher temperature metasomatic formations (apogranites, greisens, zwitteres) and indicates a significant fluorine activity in hydrothermal solutions at pre-ore stage of acid bleaching [Perry *et al.*, 1984; Rusinov, 1989].

In listvenites mica is often represented by fuchsites containing chrome in which it fluctuates in wide limits, from 0.2 to 3.5 mas.% [Sazonov, 1975]. Fuchsites of many gold-ore deposits on corresponding Al and R^{+2} in octahedric coordination approach phengites. Micas from listvenites are characterized by a bright iron coloration and usually a great dimension of the flakes (up to 3 mm). Fuchsites are found also in beresitized rocks on volcanites of medium and even acid composition in some gold and pyrite deposits. If in basic or ultrabasic chrome with listwaenitization mica is borrowed from lateral rock, with beresitization of dacites there is an obvious influx of chrome from an outer (deep) source.

Carbonates together with sericites appear as minerals typomorphic for beresites, and are wholly varied in composition. They are represented in groups: 1) dolomite –ankerite, 2) calcite, 3) magnesite –siderite and their manganese varieties. Appearance of this or of another carbonate is determined by the composition of enclosing rocks. In listvenites carbonates are usually represented by magnesites, rarely by brennerites. More ferruginous varieties are meztite,

siderite, magniosiderite, pistomesite, rare in listvenites. Carbonates of the calcite group are usually developed in outer zones of beresitization columns, which sometimes may contain a noticeable quantity of iron and manganese. Ankerite and other minerals of this group are the most universal and spread in beresites on various types of rock. Content in them of ferro-ankerite mineral does not exceed 25%, often is present a significant manganese mixture (up to 4,5 mas. %MnO).

General content of carbonates in rear zones on rocks of medium and basic composition may reach 60% of their volume. The total picture of carbonate extension, synchronous with acid leaching is complicated by the repeated appearance of later acid stages. The latest low temperature stages are present only in veins of pure calcite.

Chlorites are characteristic of outer zones of beresitization aureoles, where they develop pseudomorphically on dark-coloured minerals. Further, with the increase of metasomatic transformations, chlorites mix with ankerites or siderites and bright mica. Much more widely chlorites are spread in close association with ore minerals in the composition of ore-accompanied or post-ore veins. The composition of chlorites from beresitized rocks varies widely (fig.20.3). The diagram shows that these chlorites noticeably differ from the metamorphic in Al^{IV} content, which is lower than 1,3 but higher than 0,8 (the latter value characterizes the swollen chlorites). Ferruginosity varies within wide limits, but already in chlorites from listvenites the value of the $Fe/Fe+Mg$ ratio does not go below 0,2 [Sazonov, 1975]. As the most ferrous are observed ore-accompanied berthierites and chlorites from ore association. Iron content in chlorites is also conditioned upon sulphur activity which controls chlorite ferrosity on the following reactions:



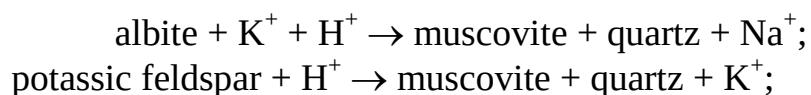
Existing analytic data, the shown Fe^{+3}/Fe^{+2} ratio in chlorites testify to a rare predominance of ferrous oxide.

The development of this or of other types of chlorite in beresites may be for ore regions typomorphic signs of a definite aspect of mineralization. For instance, in the Eastern Transbaikalian ore province the uranium deposit in hydromicaceous metasomatites is characterized by a wide extension of berthierites, but the polymetallic and gold-polymetallic deposits have normal 14A chlorites of varying ferruginosity.

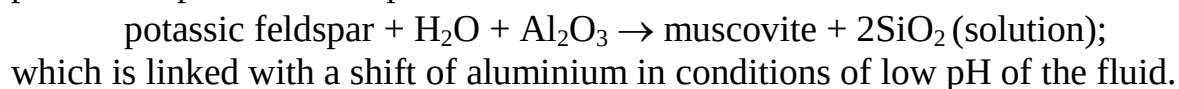
Peculiarities of chemical composition of beresites. The chemism of the beresitization process is defined by the acid character of the solution as well as by the composition of the initial rocks. For rocks of acid composition is recorded an intense removal of bases and addition of silica, water, sulphur and carbon dioxide. In the outer zones of metasomatic columns functions a removal of Ca and Mg to the extent of approaching the central zones: Fe, and then : Na. In the inner zones of quartz-sericitic composition, where disappear relicts of potassic

feldspars, may decrease the K content, and in the monoquartzitic zone occurs a full removal of K and Al. In intermediary and inner zones, at the expense of disseminated pyrite may grow the Fe content. In the course of transformation of rocks of medium and basic composition is characteristic an influx of carbon dioxide linked with massive development of carbonates. In dependence upon their composition occurs a redistribution of Ca, Mg and Fe. In intermediary and inner zones of the columns is observed a partial removal of silica and accumulation of K and Al at the expense of sericite development. Characteristic are opposite tendencies in the behaviour of SiO_2 and CO_2 : from outer to intermediate zones decreases the content of silica and increases carbon dioxide. In the inner zone silica content increases and correspondingly carbon dioxide provokes an increase of silicification.

Upon serpentinite listvenitization Si is removed, and in most columns also Al, Fe, Ni, Mg and Ca, K, C, S are added. Titanium is in most cases inert. Al, Fe, Cr, Mn in a few cases are added, linked with fuchsite and pyrite. On the whole, the direction of chemical transformation at berisitization is accompanied by removal of alkaline-earth elements and hydrolysis of feldspars according to the scheme:



Often in beresites on rocks of basic composition there is no inner monoquartzic zone. In a quartz-sericite zone may be observed sharp increase of Al and K content and abundance of sericite. Moreover sericite forms a full pseudomorphosis on feldspars:



Facies varieties of beresites. Facies of beresitized rocks are determined in dependence upon the influence of the composition of initial rocks and intensive factors, chief of which are T, f_{CO_2} , f_s , pH. Facies conditioned by the influence of the initial composition of the substratum, are represented by beresites and listvenites. The former are characteristic of altering rocks of a wide spectrum of compositions, from rhyolites and granitoids to gabbro, the second are only for rocks of ultrabasic composition or serpentinites developed on them. To this same group are related non-carbonatic facies of beresites on united alkaline-earth elements of ultra-acid granitoids.

Apart from the most widely spread quartz-ankerite-sericitic facies, to the number of facies determined by intensive parameters, are related calcite-sericite, sericitic-chlorite-calcite facies (low pH and f_{CO_2}) and hydromica-quartzic facies (low temperature).

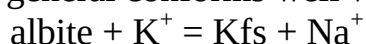
Facies of quartz-ankerite-sericite metasomatism (substantially beresites) represent the most spread type of hydrothermal medium-temperature perior

transformation. The chief typomorphic sign is the development of inner zones of parageneses of quartz with sericite, ankerite and pyrite.

According to B.I.Omelianenko [1978] to each metasomatic facies corresponds a determined type of metasomatic columns. The zoning present below reflects the basic tendency to metasomatic transformation in granites: 1) granite-quartz, potash feldspar (pfs), oligoclase, biotite, amphibole, titanomagnetite; 2) feebly altering granite, quartzite, potash feldspar, albite, calcite, chlorite, dolomite, sericite, pyrite; 3) beresitized granite, quartz-sericite, potash feldspar, ankerite, pyrite; 4) beresite, quartz, sericite, ankerite, pyrite; 5) quartz, sericite, pyrite (inner zone of full silicification is observed rarely enough).

The general direction of the metasomatism process does not depend upon the composition of the rocks. As an example of alteration of rocks more basic than granites may serve beresitized diorites of the uranium deposit Ishimskoe in Central Kazakhstan (fig.20.4), where beresitization ends in the formation of an inner quadrimineral zone of quartz+sericite+ankerite+pyrite.

In the development of hydrothermal transformation on bifeldspar rocks plagioclase most often dissolves first, the potassic feldspar (kfs) is much more stable, and its relicts are often preserved in inner zones, even in contact with ore veins. This manifestation in general conforms well with data on equilibrium



At 300°C the constant of equilibrium nears 1, but sharply grows with the sinking of temperature, which increases the stability of kfs relatively to albite. A reverse correlation corresponds to beresites of higher temperature, in which are noticed sodic micas (paragonites) [Sazonov, 1979; Grabezhev, 1995].

The facies of listvenites is less spread than the quartz-ankerite sericitic, and coincides with serpentized ultrabasic rocks. Listvenites are characteristic of gold-sulphid deposits of the Ural, Altaï, Sayan and other regions. In foreign literature these rocks are described as quartz-carbonate magnesite metasomatites, but also under the name of “duelo”, “virginite”. Listvenites are met in homogenous rocks, forming zonal aureoles, as well as in contact of various surroundings, for instance of granites and serpentines. Typomorphic minerals of listvenites are ferro-magnesian carbonates (breunnerite, magnesite, dolomite, parankerite), fuchsite, pyrite. Quartz is less significant. A source of chrome for fuchsite are chrome-spinelites, incoming in the composition of ultrabasic rocks. Initially, according to V.V.Nikitine, B.Pkrotov, A.N.Zavaritsky hydrothermal transformations of ultrabasic rocks, replaced by breunnerite, quartz, potassic mica (fuchsite) were called listvenites. Talc is not observed in compositions of synchronic zoning. A typical metasomatic column of listvenitization, with a general thickness of altered rocks not greater than 25m, has the following aspect [Borodaevsky and Borodaevskaja, 1947, Borodaevsky, 1958, Sazonov, 1975]:

1. “Grey” listvenite on serpentinite or talc-carbonatic metasomatite: breunnerite or dolomite, quartz, chromite, pyrite. 2. “Ferrous” listvenite: breunnerite, ankerite (the zone does not exist everywhere).

V.N.Sazonov [1979] has obtained data of definition of K-Ar growth for granite-porphyrite and fuchsite-containing listvenites developed in them, which indicated a genetic link of the latter with granite porphyries.

In hydromicaceous facies exist mixed-layered mica-smectites and hydromicas instead of sericites. Other differences from beresites are reduced to the decrease of pyrite extension and increase of hematite, and also to a large development of berthierites, mixed-layered chlorite-smectites. From their argillites differs the absence of metasomatic kaolinites and smectites.

In the limits of some deeply laid open deposits of acid type with increasing depth is traced a mixture of hydromicaceous metasomatites with typical beresites in the limits of single aureoles of hydrothermal transformation and coinciding with one the same solution-producing structure [Andreeva *et al.*, 1996]. Isotopic K-Ar datation, adduced on dispersed micas of the Streltsov uranium deposit, the biggest uranium deposit of Russia, reveals a superficially identical growth value for all the interval of deeply laid open ore-bearing zones (table 20.1). Thus, the

Table 20.1. Results of isotope K-Ar datation of dioctahedric dispersed micas from metasomatic various hydrometric levels of the Antei-Streltsov deposit

Depth of chosen samples, m	Content of swelling mixed layer, %	K, %	$^{40}\text{Ar}_{\text{rad}}$, ng/g	Growth, in 1000 years	Enclosing rock
190	8-10	5,24	51,0	136±6	Trachydacite
250	6-8	6,22	84,8	130±5	Trachydacite broken down
320	8-10	6,70	67,2	139±6	Basalte
430	10-12	6,87	66,	134±5	Granite
598	6-8	6,40	157,8	129±5	Granite broken down
1031	6-8	6,12	59,1	134±5	Granite
1070	<5	6,98	69,5	138±5	Granite
1422	6-8	7,28	68,8	134±5	Granite
1596	5-7	5,84	57,9	138±6	Granite
2145	0	6,80	65,0	133±5	Granite
2161	0	7,63	74,0	135±5	Granite

beresitic and hydromicaceous type of alteration does not have precise boundaries; sometimes they coexist with the limits of one deposit and a single metasomatic aureole; they can therefore be maintained in the composition of one family.

Ore-accompanied metasomatic and veinous formation in beresites. To ore-accompanied are related mineral associations formed simultaneously or nearly at the same time with the deposition of ore minerals. They are spatially very closely linked with ore. Of ore-accompanied metasomatites, as was already established by D.S.Korzhinsky, is typical the gathering of minerals, the composition of which is in a significant measure conditional by chemical components leached from enclosing rocks in the process of their hydrothermal transformation.

Metasomatites of acid bleaching type of beresites in the composition of ore-accompanied associations are characterized by chlorites, berthierites, carbonates (mainly ferriferous and magnesian-ferriferous), pyrite, hematite, albite, adular, fluorite. These minerals are spread in veins as well as in metasomatic form, laying borders, edgings on the periphery of accumulation and veins of ore minerals. The thickness of the manifestation of these metasomatites is usually interrelated with the power of ore bodies, but much smaller than the thickness of aureoles of beresitization. A very important peculiarity of these transformations consists in the full absence of zoning, which undoubtedly testifies to the distinct disequilibrium of the whole process of acid mineral transformation (including periveinous metasomatism), following a stage of acid leaching.

Chloritization is known practically on all deposits, sulphidic, gold-ore uranium, molybdene-uranium, fluoritic. Chlorite accumulations, sometimes nearly monomineral, form uneven zones of thickness of up to tens of centimetres, bordering ore bodies. Chlorite deposition may come significantly later than relatively important ore stages. The predominant type of chlorites usually depends upon facies of metasomatites: in beresites develop ferrous and magnesian-ferrous chlorites and in hydromicaceous metasomatites, ferrous berthierites or swelling chlorites.

Albitic ore-accompanied transformations were for a long time studied in uranium deposits [Andreeva & Golovine, 1979; Naumov, 1985], but later albite was discovered in some metasomatic gold-ore deposits [Moissenko *et al.*, 1978; Rusinov *et al.*, 1996]. An example of development of albite metasomatites is the Streltsov uranium deposit, where these transformations are developed in various rocks of effusive thick cauldrous and granitoid substratum (fig.20.5). The thickness of the zone of veinous metasomatic albitization isn't great and only in granitoids can they reach the first metres, tracked down to a depth of 1800m. Albite corrodes and mixes with hydromicas, rock-forming potassic feldspar and plagioclases. Quartz mixes with albite only in areas of maximal interaction.

Na₂O content in albitized dacites may reach 7%, in granitoids up to 10 mas.%, but content of trivalent iron in albitites is of 1-2% relatively to the initial rocks. Hematite-albitic metasomatites always contain increased concentration of uranium, basically in the form of urano-titanates.

In the limits of sulphid gold-ore deposits, metasomatic-veinous albite is displayed only on deep and medium horizons and also near in time to chief ore stages.

Paragenetic analysis and basic physico-chemical parameters of beresitization. Mineral parageneses of beresites are determined above all by temperature conditions, rock composition and CO₂ activity. According to definitions given by D.S.Korzhinsky, the conditions of beresite formation are at rather low temperatures, at which there are stable parageneses of carbonates with potassic mica in the absence of calcic silicates.

Available data of study of fluid inclusions display a significant T_{hom} dispersion, but quartzes, which maximally approach in time the formation of zonal aureoles of metasomatites, are characterized by temperatures of 280-320°C and pressure up to 1 kb. For the determination of T-P conditions of beresitization are also utilized various mineral thermobarometers: dolomite-calcitic, muscovite-chlorite, plagioclase-muscovite, breunerite-ankerite. According to these data, beresitization temperature oscillates between 490-350°C at pressure of lithostatic burden [Sazonov, 1984] or corresponds to a wider temperature interval of 450-250°C with pressure from 0,5 to 2 kb [Martynov, 1992].

Surface temperature limit of beresitization according to these data is somewhat increased. So, with an experimental modeling of beresitization [Shapovalov & Zarskiy, 1978] it was established that its surface temperature limit, although it depends in a significant degree upon carbon dioxide, all with a high enough share of XCO₂ = 0.2, does not exceed 380°C. Above this temperature there develop quartz-sericitic metasomatites, or, in alkaline milieu, gumbesites. And higher temperatures do not promote stability of ferrous carbonates, particularly of carbonates in the order of siderite-magnesite. According to experimental data of several authors, temperature stability of magnesian-calcic carbonates grows correspondingly in the magnesite → dolomite → calcite order. With this association of quartz with magnesite with a share of carbon dioxide, equal 0,2, stable at a temperature not above 300°C, but the dolomite association not above 380°C.

The lower temperature limit of beresitization is conditioned by displacement of sericite by mixed-layered minerals of micasmectite type and other clayey minerals. Temperature regulation of the stability of hydromicas and adaptation of micasmectites to high content of mica layers is difficult to evaluate inasmuch as they present themselves as metastable formations. Available data of direct observation of contemporary mineral formation in thermal fields indicate

manifestation of non-swelling illites already at a temperature of 210-220°C [Muffler & White, 1969]; Cathelineau, 1988]. According to experimental researches on beresitization, at temperature of 250°C and higher, mixed-layered phases are not fixed, but calculated data [Redky & Omelianenko, 1983] on the model K-Na-Si-Al-H₂O-NCl system show the possibility of formation of mixed-layered illite-smectite already at 250°C. Apparently, to this temperature may be counted the lowest temperature limit of beresites. Hydromicaceous metasomatites correspond to the interval of roundly 230-250°C.

At lower temperatures, metasomatic columns are formed with participation of smectites and mixed-layered illite-smectites with a great content of swelling interlayers (rectorites and rectorite-like phases) and kaolinites.

Hydrothermal solutions, called beresitization have a complex cationic and anionic composition. Data of study of flow inclusion in vein carbonates and quartzes [Sazonov, 1984] show the constant presence of Na⁺, K⁺, Ca⁺², Mg⁺², HCO₃⁻, Cl⁻, rarely of SO₄²⁻, F⁻; in gaseous phase of inclusion are present H₂O, CO₂, N₂; Na⁺ always predominates on K⁺. CO₂ content in inclusions of vein minerals oscillate within wide limits, and sometimes carbon dioxide occupies almost the whole volume of the vacuum. From model experiments it is known that with X_{CO2} values about 0,01 in altering rocks is calcite noticeable, and ankerite is observed only if this value exceeds 0,05. Metasomatic zoning of usual beresites develops with the value of carbon dioxide about 0,1.

Carbon dioxide fugacity at constant temperature has a decisive influence on the growth of ferruginosity of carbonates towards inner zones of metasomatic columns, which is a nearly general manifestation. This impartially for the dolomic-ankerite and magnesian-siderite. Extension of carbonate ferruginosity in this direction is promoted by the growth of acidity of the milieu, and a diminished activity of magnesium compared to iron [Korenbaum, 1967; Sazonov, 1984; Martynov, 1992].

The dependence of parageneses of inner metasomatic zones upon intensive parameters is illustrated on a diagram (fig.20.6). They give the possibility of evaluating the possible variation of solution in relative concentration of potassium and carbon dioxide and the possible T-P conditions. Potassium content ought to correspond to the value of the ratio $\lg(aK^+/aH^+) = 1,5-2,5$. Otherwise, at less than 300°C, sericite ought to mix in the rear zones of the kaolinite columns. Above 320°C beresites give way to non-carbonatic quartz-sericitic metasomatites, analogous to low temperature greisens. In higher concentration of potassium and increasing temperature beresites turn into gumbesites.

Growth of pressure (with constant carbon dioxide concentration) favours reactions of carbonatization, with which the formation of carbonates ought to go on in a succession of calcite → ankerite → breunerite. However, as far as beresites are related to metasomatites principally of one hypabyssal facies of

depth, pressure variations at beresitization are immaterial. Moreover, the enumerated order of carbonates often does not correspond to the vertical zoning of beresites observed in real conditions. Mineral associations with calcites does not characterize near-surface horizons but the deepest ones, and ankeritic and breuneritic associations characterize the superficial and middle ones. This peculiarity is mostly observed in metasomatites with significant vertical amplitude of mineralization (fig.20.7), linked with the existence of a vertical temperature gradient, which is strengthened by a distinct replacement depth of hydromicas and illite-smectites by non-hydrated sericites. The values of surface pressure, which are sometimes based on data of research on fluid inclusions in veinous minerals, are related to later veinous stages of mineral formation and may be linked with tectonic constraints already in postmetasomatic periods of development of a hydrothermal system.

Significance of beresites as periore rocks. With beresites are linked many ore deposits of uranium, polymetals and gold. Beresites may even be mentioned as metasomatic family, typomorphic of polymetallic and gold ores. In these cases, when polymetallic ores are spatially associated with higher temperature metasomatic formations, for instance with skarns, a detailed research always indicates a later development of beresite parageneses (or listvenites). Low temperature facies of beresites (hydromicaceous metasomatites) are typomorphic of deposits of uranium and fluorite.

Mineralization in beresites is related to a connected type, on the localization of any ores regularly linked with a horizontal and a vertical metasomatic zoning. Rich ore, as a rule, coincide with the inner zone of a metasomatic column in its section of their greatest thickness. Ore bodies may also be localized outside the limits of the inner zone, but sometimes they do not leave the zonal aureoles of beresitization. Practically in all cases of appearance of ore mineralization are traced accumulations of ore-accompanying minerals, chlorite, carbonates, berthierite, albite, adulare, sericite of $2M_2$ modification, etc, the formation of which occurs after a stage of leaching. Their secretion has a combined metasomatico-veinous character, but the intensity of their development is nearly always proportional to the scale of mineralization. In practical relation the level of manganosity of the carbonates, is very marked as far as they are wholly characteristic precisely of a Pb-Zn and Au-Ag-Pb-Zn deposit, in which the manganese activity habitually increases in the last stage of development of the hydrothermal process, at the moment of ore deposition [Rusinov, 1989].

Localisation of ore bodies relatively to vertical metasomatic zoning is regular. Industrial accumulation of ore minerals is never fixed on upper or lower tapering out of the general aureole of beresitization, but gravitates to places of maximal thickness in the superficial part of the aureole. As one of the signs of the presence of ore mineralization may serve such a degree of development of

metasomatic carbonatization, which depends upon fullness of manifestation of transformation and a corresponding deep erosion section. The carbonate/(quartz + sericite) ratio with similar composition of initial rocks proves to be a direct indicator of depth [Sazonov, 1984].

The extension of carbonates in vertical zoning proceeds along two schemes. The first one corresponds to a decrease, from deep to superficial horizons, of the content of ferrous carbonates in the outer and intermediate zones of beresite column and an increase of the quantity of calcite. This condition corresponds to an insignificant temperature gradient, and the replacement of calcite-containing parageneses by ankeritic ones may occur with an increase with depth of the carbon dioxide fugacity from $-0,5$ to 1 [Rusinov, 1989]. There often occurs another variant, when associations with calcites are observed on deeper horizons compared with ferrous carbonates. Such correlations are linked with a significant vertical gradient of temperature, which is usual to beresites of hypabyssal and subvolcanic facies of depth. This is also true of the hydromica facies (cf.fig.20.7). Maximal concentration of useful components gravitate to intervals of development of ankerite-containing parageneses.

In the mentioned Streltsov uranium deposit at deep hypsometric levels, where occur calcite-sericitic and dolomite-sericitic parageneses, ore bodies are absent and only narrow zones are seen of increased radioactivity.

So, the scale of development, facial composition and vertical zoning of beresitized rocks prove to be indicators of the type and scale of mineralization and assist in evaluating perspectives of extension of mineralization in depth.

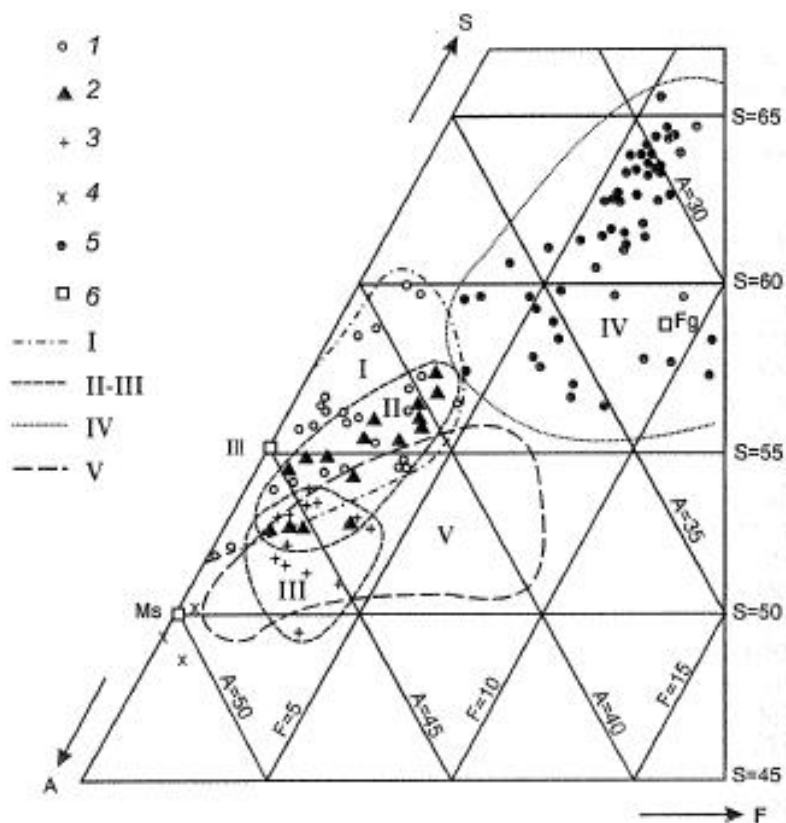


Fig. 20.1. Composition of hydrothermal sericites and hydromicas in coordinates A(Al)-S(Si)-F(Mg+Fe+Mn).

1– calcic micas and mixed-layered illite-smectite from argillisites and hydromicas; 2 – micas from beresites; 3–micas from Ural beresites; 4 – from corundum-containing secondary quartzites; 5–from sedimentary rocks at various stages of epigenesis; 6–points of end-member minerals: Ms – muscovite, Ill – illite, Fg – phengite, Lf – leucophyllite. Contours of field of composition of micas of various genesis: I–mica from argillisites and hydromicatites, II– and III– mica from beresites, IV– sedimentary epigenetic mica, V– metamorphic mica of facies of low and moderate pressures.

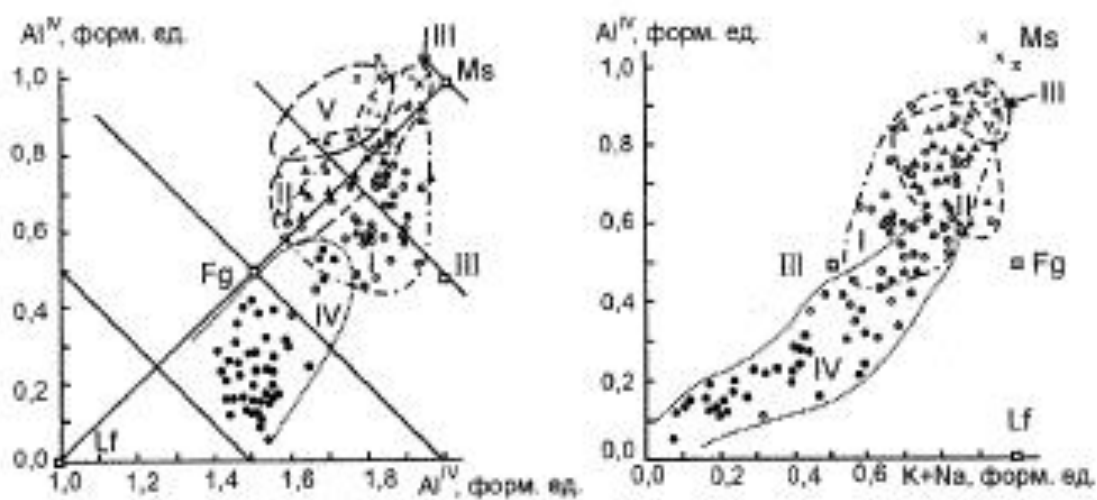


Fig. 20.2. Composition of sericites and hydromicas in dependence upon Al distribution on positions (a), composition of sericites and hydromicas of various genesis in Al^{IV} -K+Na coordinates (b).

Notation is the same as on fig. 20.1.

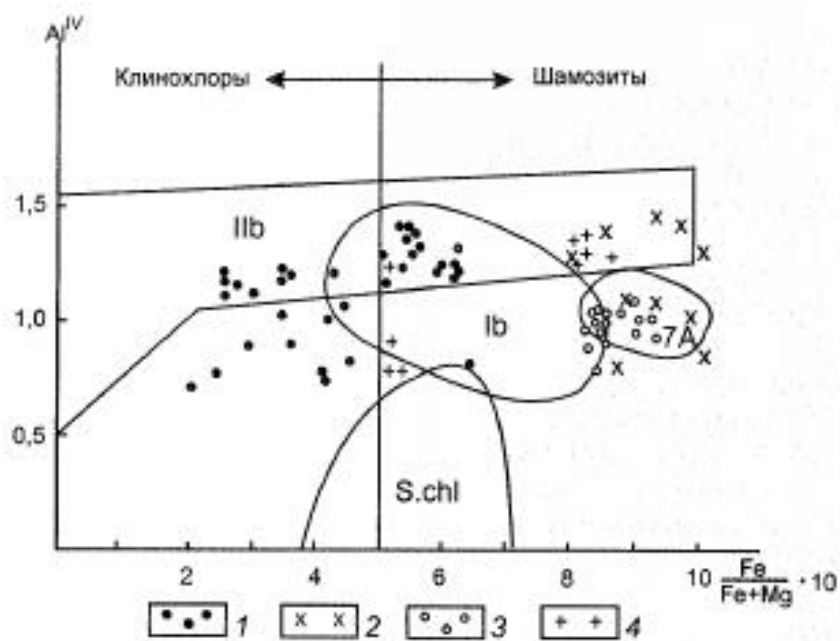


Fig. 20.3. Diagram of compositions of hydrothermal chlorites in Al^{IV} -Fe/Fe+Mg [Curtis et al., 1985; Jahren & Aagaard, 1989; data of O.V.Andreeva].

Ilb–field of composition of metamorphic chlorites with predominant polytype; Ib–chlorite from sedimentary rocks; 7A– bertierites, S.chl – swelling chlorites. 1– chlorites from periere beresites, 2–bertierites from gold deposits; 3–bertierites from uranium deposits; 4– ore-bearing 14A chlorites.

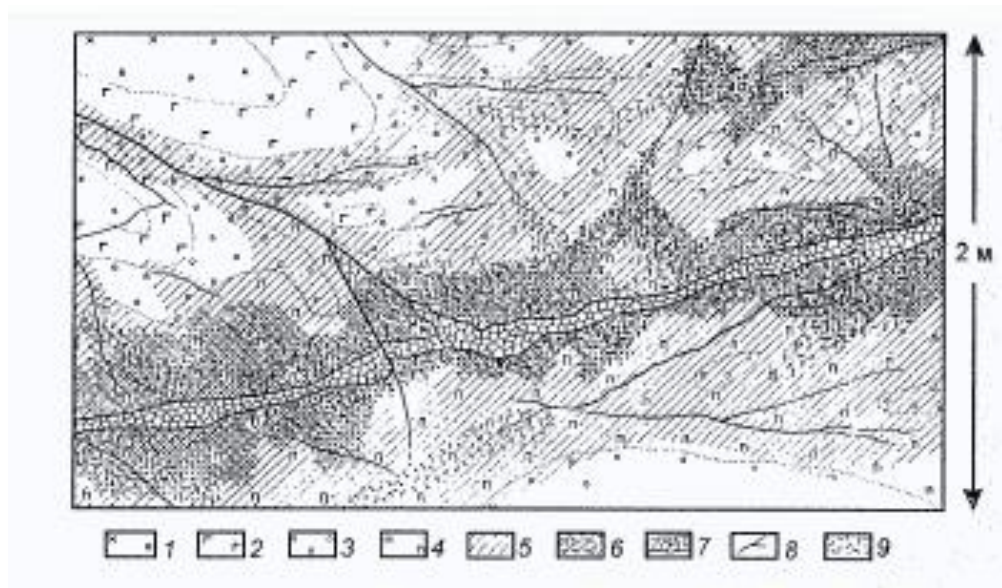


Fig. 20.4. Outline of structure of aureoles of beretisation near an ore-bearing zone. Uranium deposit of Ishim, Kazakhstan, documentation of walls of ort???? by B.I.Omelyanenko [Zharikov & Omelyanenko, 1965].

1-porphyry diorite, unaltered; 2-feebly beresitized porphyry diorite (albite, carbonate, chlorite, quartz, sericite, pyrite); 3-beresitized diorite (carbonate, albite, quartz, pyrite); 5-intensively pyritized rocks; 6-areas of development of veinlet-disseminated uranium deposit; 7-areas of brecciation; 8- break dislocations; 9- zones of fracturation.

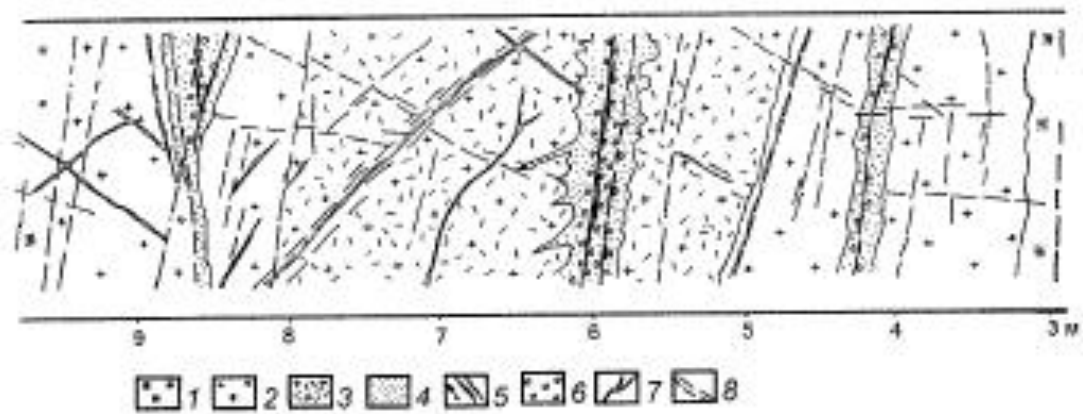


Fig. 20.5. Character of development of hydromicaceous metasomatites and albitic ore-bearing formations in granites of Streltsov uranium deposits (East Zabaikal) (after V.A.Golovine).

1—coarse-medium grained biotite granite; 2—small dimension granites of composition Qtz+Kfs+Ab+H-mic+Ank+Hem (Ls) and Qtz+Kfs+H-mic+Ank+Hem; 3—intensively altered granites Qtz+H-mic+Ank or Qtz-H-mic; 4—veinlet-metasomatic albite; 5—uranium mineralization; 6—areas of development of ore-bearing hematitization; 7—veinlets of chalcedonomorphic quartz; 8—break dislocations, zones of fracturation.

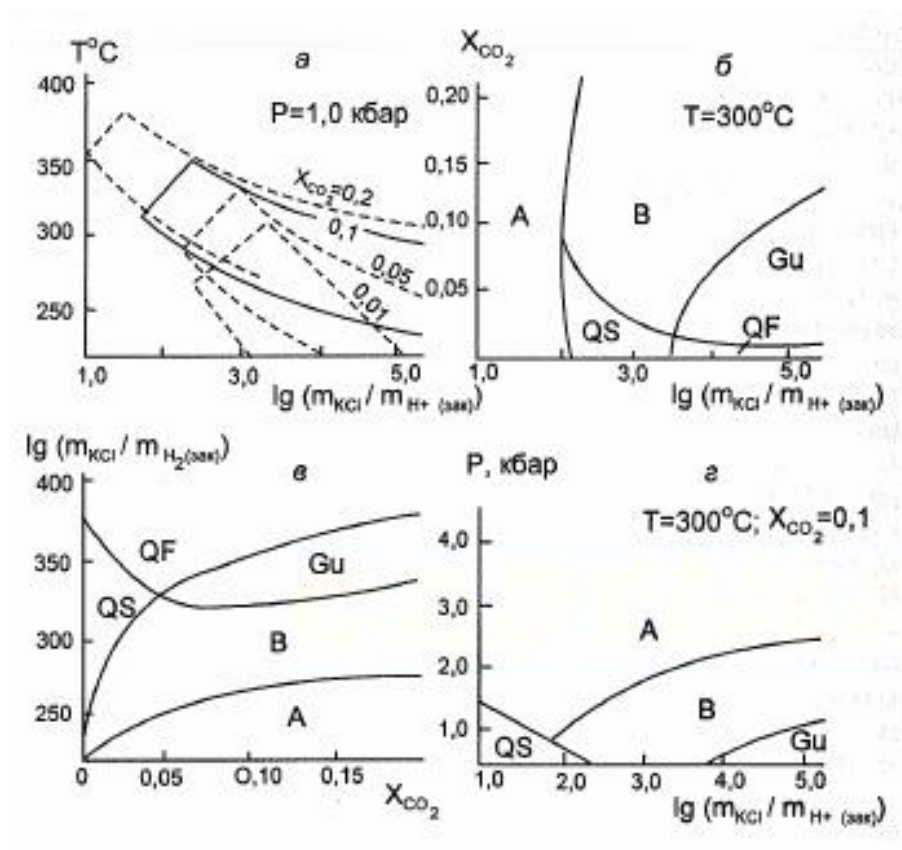


Fig. 20.6. Boundary conditions of formation of beresites (B) relatively to gumbeites (Gu), argillites (A), quartz-sericites (QS), and quartz-feldspars (QF) of metasomatites in dependence upon: a - T - $\lg(m_{\text{KCl}}/m_{\text{H}^+(\text{ref})})$, b - X_{CO_2} - $\lg(m_{\text{KCl}}/m_{\text{H}^+(\text{ref})})$, c - T - $\lg(m_{\text{KCl}}/m_{\text{H}^+(\text{ref})})$, d - P - $\lg(m_{\text{KCl}}/m_{\text{H}^+(\text{ref})})$, law, composition of solution of late chilling [Shapovalov & Zارايسкий, 1978; Zараиский, 1989].

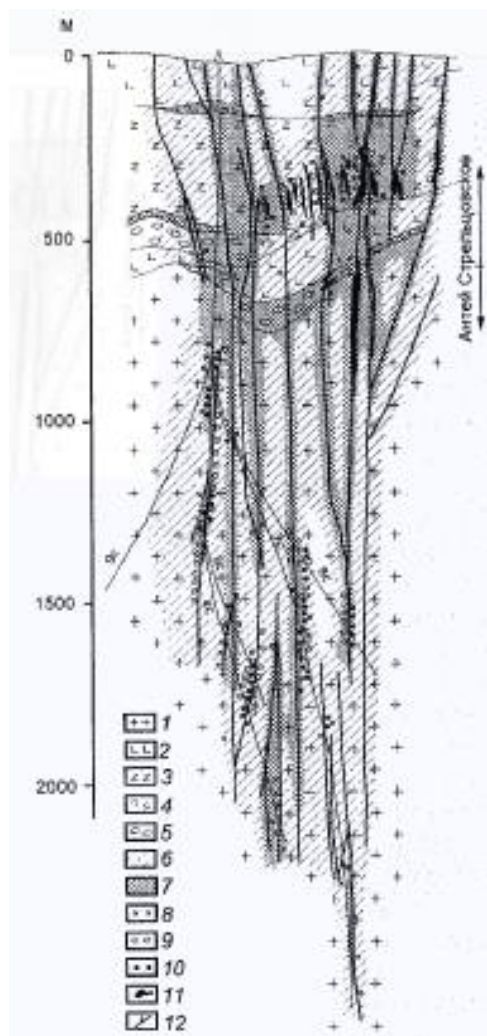


Fig. 20.7. Aureoles of extension of perior transformation in the Streltsov uranium deposit (in material of L.P.Ischukova, A.G.Evstratov and own data).

1–granitoids; 2–basalts, andesito-basalts; 3–trachydacites; 4–tufas; 5–conglomerates, gravels, sandstones; 6–zones of weak hydromicatization and beresitization; 7–zones of intense hydromicatization and beretization; 8–portions of development of ore-bearing chlorites and bertierites; 9–ore-bearing albitization; 10–areas of development of disseminated uranium mineralization; 11–ore bodies; 12–dislocation breaks. Sericite and 14A chlorite begin predominating at depths of 1600 to 1800m.

CHAPTER 21

Alkaline metasomatites

The chief properties of alkaline metasomatites are: increase of alkaline content in the rock; formation of minerals in conditions of high activity of the alkali; predominance of addition of components over removal, decrease of porosity and permeability of the rocks. In the process of alkaline metasomatism there occurs a linkage of alumina with containing rocks in feldspars, rarely in nepheline, zeolites, leucite. Here are considered only the most spread metasomatites, in which alumina-containing minerals are represented by feldspars. Mineralogical criteria of alkaline metasomatism are the replacement of quartz by albite and (or) potassic feldspars, but also by alkaline amphiboles and (or) aegyrine. It must be noted that the formation of the indicated minerals with stability of the quartz testifies only of the high alkaline content of the solutions, but does not prove their alkaline character. One distinguishes two groups of formation of alkaline metasomatites: the sodic and the potassic. In the extension in the rock sodic alkaline metasomatites substantially predominate over potassic. As type of transition is distinguished the formation of sodico-potassic (bifeldspathic) metasomatites.

The chief property of sodic alkaline metasomatites is the wide development of albite in them. In connection with them, sodic metasomatites of various formations are quite often described under the name of “albitites”. This term undoubtedly is wider than a family, and without supplementary typomorphic signs does not permit determining the metasomatites.

As to temperature of formation sodic metasomatites are divided into those of medium temperature and those of low temperature. The first ones, together with albite, are characterized by the development of aegyrine, alkaline amphiboles, micas, epidote; the other ones, by carbonate and chlorite.

Medium-temperature sodic metasomatites are represented by three family types: albitized granites, sodic metasomatites of contact zones of nepheline-

syenitic massifs, and sodic metasomatites of zones of fracture of precambrian basement.

Low temperature sodic metasomatites are represented by the formation of aceites.

21.1. Family of albitized granites.

Definition. Albitization is one of the most widely spread processes of postmagmatic alteration in the granitoids. In an overwhelming majority of cases it is relatively feebly developed and manifests itself in perthitization of potassic feldspar with formation of chessboardic and fringe albite. Intensive occurrence of albitization with formation of ore-bearing albitites is recorded only in connection with intrusions related to much later phases of granitoid complexes. According to P.V.Koval [1975], collecting materials on a great number of massifs of albitized granites, their share forms not more than 1% compared with the whole area, occupied by granitoids of the corresponding assemblage. Consequently the great accumulation of sodium in residual solution may be considered as property of postmagmatic processes, conditioned by specific compositions of highly differentiated magmas.

The term *albitized granites* in a sub-familly sense was propounded by P.V.Koval [1975] and we think it is the most successful. In many publications albitized granites are described by the name of “apogranites”. This term was suggested by A.A.Beus in connection with granites substantially transformed in postmagmatic processes in which, apart from sodic metasomatism, quite often also occur potassic feldspathization and greisenization. Thus, the term “apogranitic” unites metasomatites relative to three metasomatic formations, which are often spatially combined. No information whatever on the relative role of the different processes and intensities of metasomatic transformation is carried by the term “apogranite”. Albitized granites also are divided under the names of albitites, rare-metal granites, lithic-fluoritic granites and others. The most characteristic sign of granite albitization is the development of a great quantity of tabular and lath-like albite mixed with microcline and quartz. Below are given the chief formation peculiarities of albitized granites.

Geological setting. According to A.A.Beus [1968], albitized granites are formed on all stages of development of the earth crust. Analysis of concrete manifestations of metasomatites of this family show, however, that for them, as for greisens, is typical the phanerozoic age. Albitized granites are met either in regions of superficial folding or in the limits of platforms and intermediate massifs. Many of the massifs are linked with processes of activation of ancient structures. The regions of development of albitized granites are characterized by intense occurrence of granitoid magmatism with predominance of granites of standard geochemical type. Bodies of albitized granites are represented by typical fracture intrusions, formed in conditions of moderate and small depth.

Albitization is superimposed on dykes of granite-porphyries, intersecting parent granites. Consequently, the latter have fully crystallized at the beginning of albitization.

Regular building of zones of sodic metasomatism in vertical direction is determined by the presence of a general tendency to accumulation of intense albitization from below upwards. Intense albitization is characteristic only of apical parts of intrusives, but in depth they extend on the first hundreds of metres. In depth, control of albitites by fracture zones appears most distinctly and on any scales, from control of tectonic zones of thick and extensive parts of albitization to formation of albite along separate fractures and microfractures. The thickness of albititic bodies is usually insignificant and rarely reaches hundreds of metres. A feeble albitization has a coarse extension, occupying a great volume of the granites. Albitization is undoubtedly related to an earlier alkaline stage of a postmagmatic process. With time it gets replaced by a coarse greisenization and later by the development of perifissural greisenization [Grabezhev, 1981].

Peculiarities of mineral and chemical composition. Spatial combining of processes of potassic feldspathization, albitization and greisenization sometimes does not permit precisely to delimitate the mineral and chemical transformations, linked with the different stages of the postmagmatic process. The given circumstance substantially hampers formation of metasomatic columns. The basic mass of albitized granites is submitted to associations to the outer zones of the column consisting in albite, quartz, microcline and mica, to which are added fluorite, but also various accessory minerals. In the rocks is observed a partial replacement of microcline and magmatic plagioclase by lath-like and tabular albites. An overwhelming mass of published chemical analyses deal with this variety. The difference of chemical composition of metasomatites and initial granites is insignificant. Na_2O content grows to 1-2,5%, K_2O diminishes to 0,5-1,5%. Variations in the content of other components are not great and may be linked not only to sodic metasomatism. Non-completion of the reaction of albitization of potassic feldspar is accounted for by its relatively high content also of granites. As a result, corresponding activities of sodium and potassium in solutions are kept on level, by the corresponding stability of bifeldspar association. Full replacement of potassic feldspar by albite has been carried out only in relatively narrow zones of most intense circulation of postmagmatic solutions. In the final products of intense metasomatism of leading minerals appears albite. The second place, after albite, is most often occupied by mica. In dependence upon mica content, P.V.Koval [1975] has distinguished muscovite-lepidolitic, lepidolite-biotitic, ambligonite-lepidolitic, zinvalditic, muscovite-protolitionitic type of albitized granites. A.I.Grabezhev [1981] has described microcline-albitic metasomatites with a sharply subordinate quantity of muscovite. Quartz in them is replaced not only by albites

but also by microcline. A.A.Beus and N.E.Zalashkova have described quartzic albites formed of fine-plate albites and quartz. The correspondence between these minerals oscillates between granite proximity and significant predominance of albite over quartz.

Full replacement of quartz by albite is very rarely observed. With it are formed sacharoidal monomineral albitites. In albitized granites fluorite is usually present, the content of which varies in very wide limits. In many cases is topaz recorded. Formation of this mineral in conditions of high alkalinity presents itself as unlikely and, apparently, it occurs at stages of increased acidity.

Data of chemical analyses testify to the fact that albitization of granites is accompanied by addition of sodium and alumina and removal of silica and potassium (table 21.1).

Table 21.1. Chemical composition of initial and albitized granites in % en weigh [Koval, 1975]

Components	Granite				Albitite
	Bi-micaceous	Musco-vite	Albitized		
			moderate	strong	
SiO ₂	74,24	78,83	75,87	71,90	69,27
TiO ₂	0,20	0,16	0,08	0,03	0,00
Al ₂ O ₃	13,27	13,16	12,74	15,74	17,33
Fe ₂ O ₃	0,55	0,93	0,38	0,57	1,36
FeO	1,04	0,88	0,72	0,38	0,54
MnO	0,03	0,05	0,13	0,05	0,11
MgO	0,10	0,28	0,22	0,13	0,12
CaO	0,87	0,99,	0,55	0,49	0,55
Na ₂ O	4,01	3,31	4,73	6,50	9,69
K ₂ O	5,07	4,69	4,07	3,29	0,30
Rb ₂ O	-	-	0,08	0,11	0,01
Li ₂ O	-	-	0,01	0,01	-
P ₂ O ₅	0,09	0,05	0,04	0,03	0,03
Loss. Ign.	0,50	0,71	0,50	0,56	0,41
F	0,13	0,15	0,11	0,05	0,04

Horizontal metasomatic zoning occurs very indistinctly. Several authors have adduced metasomatic columns which in great measure are characterized by the direction of the process, rather than by really documented metasomatic zoning. The most real are the following types of columns:

I 0) Quartz + microcline + oligoclase + biotite; 1) quartz + microcline + albite + muscovite; 2) quartz + albite + muscovite; 3) albite + muscovite;

- I. 0) Quartz + microcline + oligoclase + biotite; 1) quartz + microcline + albite + muscovite; 2) quartz + albite + muscovite; 3) albite + quartz; 4) albite;
- II. 0) Quartz + microcline + oligoclase + biotite; 1) quartz + microcline + albite + muscovite; 2) microcline + albite; 3) albite.

Recorded facies of albitized granites are forming in conditions of very high sodium activity. They are characterized by development of aegirine and alkaline amphiboles, and sometimes astrophyllite.

Metallogenic and geochemical specialization. To albitized granites are related industrial concentrations of beryllium, tantalum, niobium, lithium, zirconium, rare earths, tungsten and tin. The characteristic ore minerals are beryl, euxenite, bertrandite, phenakite, columbite, microlite, pyrochlore, fergusonite, zircon, wolframite, cassiterite and a few others. The brightest geochemical property of albitized granites is the accumulation in them of fluor, radio-active elements, increased relation of sodium to potassium. Zones of increased concentration of niobium, tantalum and zirconium get sufficiently clearly revealed with the help of radio-active appliances, so that the content in them of uranium and thorium reaches hundredths of mass %. Despite the available numerous radio-active anomalies, industrial accumulations of uranium and thorium in albitized granites are not established. In the process of albitization also are dug up hafnium, rubidium, caesium, barium and phosphorus. Concentration of these elements in metasomatites was roundly of a higher order than in unaltered granites. It was established that the greatest concentration of the foregoing elements was characteristic of metasomatites corresponding in composition to the intermediate zones of a metasomatic column. They are replaced by albite, quartz, microcline and mica. In albites the content of rare elements diminishes. Coincidence of the maximum of ore mineralization with a definite zone of a metasomatic column testifies to the synchronism of the process of albitization and ore-formation. The cause of ore deposition, apparently, is the neutralization of alkaline solutions in their mutual reaction with granites.

Conditions of formation. A thorough analysis of thermometric data shows the most probable value of albitization temperature in the 520-460°C interval. Pressure corresponds to conditions of depth in the order of 1,5-2,5 km [Koval, 1975]. The results of the study of gas-liquid inclusion with calculation of petrographic and experimental data show that albitization occurs under the influence of hydrocarbonate-sodic solutions with general mineralization of 10-15 mas.%. Content of carbon dioxide is of tens of grams to the litre. Amongst cations is sharply predominant sodium, amongst anions, carbonic, hydrochloric, fluoride-hydrogen and silicic acidity. Undoubtedly increasing alkalinity of the

solutions is determined by their soda composition. Instead, albitized solutions are characterized by a high concentration of fluor, whose complex combination plays an important role in the transfer of elements.

21.2. Family of sodic metasomatites of the contact zones of nephelinic-syenite massifs.

In connection with intrusives of nephelinic syenites there widely occur postmagmatic processes. Their temporal succession is reflected in the following order: potassic feldspathization; albitization; low temperature metasomatism (liebeneritization, sodalitization, zeolitization, carbonatization). Concerning the scale and intensity of manifestation the leading place belongs to albitization, which is linked with an accumulation of valuable elements. The final products of albitization are dealt with in the literature under the name of albitites. Transformation of nephelinic syenite into albitite is accompanied with addition of silica, in connection with which albitization relatively to nephelinic syenites may be considered as at acid stage. In relation to parent rocks albitization occupies the same situation as does greisenization relatively to granites. Instead, the mutual reaction of albitized solutions with intermediate quartz-containing rocks is accompanied by sodium addition, removal of alkali, full replacement of quartz by albite and other minerals formed in conditions of increasing alkalinity. Therefore in relation to quartz-containing intermediate rocks albitization proves to be a typical manifestation of alkaline metasomatism.

The geological setting of sodic metasomatites is determined by their narrow spatilo-genetic link with massive nephelinic syenites. The latter's formation occurs under various geodynamic regimes [Andreeva & *al.*, 1984]. A necessary conditions of the manifestation of alkaline magmatism is the destructure of earth crust consolidated in platform as well as in folded domains. Such conditions arise at all stages of geological development of the earth crust on the latter's extension to about 2,7 billion years. Most favourable to the development of alkaline rocks are structures of deep tectono-magmatic activation.

Processes of albitization occur mainly in a contact zone of nephelinic syenite massifs wide a few hundred metres, occupying a zone of exocontact, apophyse and dykes and also of rocks enclosing them. The most intense albitization occurs in portions of contact characterized by the presence of various dislocation fractures and other structural elements, controlling the movements of albitizing solutions. With the various dislocation fractures are linked linear bodies of metasomatites characterized by a clearly expressed metasomatic zoning.

Mineral properties and chemical composition. A general property of albitized nephelinic syenites is the development of the fine lamellar albite (cleavelandite). Content of anorthitic molecules in metasomatic albite does not

exceed 5%. The dimension of its crystals (0,2-0,3 mm) does not depend upon that of the initial minerals, in connection with which sacharoid albites are formed at the expense of fine-crystal syenites and of pegmatoid varieties of nephelinic syenites. Of relict minerals in albitites the greatest part is nepheline. Their replacement by albite proceeds through gradual increase of the quantity of inordinately orientated inclusions of cleavelandite. Rocks distinguished in the Octiabrskoe alkaline massif under the name of mariupolites, present themselves as substantially albitic rocks with aegyrine and relict nepheline. In correspondence with the quantities of sacharoid albite and nepheline may be estimated the intensity of the metasomatic process. In final products of albitization the content of albite reaches 95-97% of the volume of the metasomatites.

The most characterized of the dark-coloured minerals of albitized nephelinic syenites is aegyrine. Its quantity is directly proportional to the content of lepidomelane and other iron-containing minerals in the initial rocks. In most cases aegyrine is isolated in the aspect of inordinately oriented elongation of crystals measuring from a fraction to 5 mm, distributed in albitites highly invariantly. There are radiant aggregates of coarse crystals ("aegyrinic suns"). Content of acmitic molecules ($\text{NaFe} + \text{Si}_2\text{O}_6$) in metasomatic aegyrine always exceeds 70%. With these it is distinguished from magmatic pyroxenes, which usually present aegyrine-augites.

Sometimes instead of aegyrine in albitites dark mica is present. Particularly spread are micaceous albitites in the alkaline massifs of the east-Ural elevation. According to E.M.Eskova [1976], mica from albitites differs from magmatic mica by lesser ferruginosity (which testifies to decrease of the alkaline process) and in most cases there are ferriphlogopites. Its content in albitites does not usually exceed 5%. A characteristic property of micaceous albitites is the wide participation of microcline in their composition. Although in the final products of albitization albite always predominates over microclines, the latter's full replacement by albitites is very rare.

In a series of cases there is superimposed on albite mineralization of later stages of a postmagmatic process. The latter minerals are liebenerites, calcites, zeolites, fluorites. With calcitization is sometimes linked collective crystallization of accessory minerals, partially zircon.

Final products of sodic metasomatism in zones of exocontact nepheline-syenite massifs are also albitites. The predominating dark-coloured mineral is aegyrine, more rarely ferriphlogopite. In exocontact of the Djilisuiskoe massif (Altai range) are seen astrophyllite-bearing albitites, formed at the expense of fenitized aleurolites. The latter reflects stellate aggregates of aureate crystals of 2 cm diameter, whose albitite content reaches 15%. The compositions of astrophyllite corresponds to the following formula: $(\text{K}_{0,82}\text{Na}_{0,64}\text{Ca}_{0,15}\text{Mn}_{0,39})(\text{Mn}_{0,29}\text{Mg}_{0,16}\text{Fe}^{++}_{2,12}\text{Fe}^{+++}_{0,07}\text{Al}_{0,37})_{3,01}[\text{Ti}_{0,78}\text{Nb}_{0,07}\text{Fe}^{+++}_{0,15}][\text{Si}_{3,73}\text{Al}_{0,27}]$

$[\text{OH}_{1,78}\text{F}_{0,22}]_2 [\text{OH}_{1,37}\text{O}_{12,63}]_{14}$. Dissimilar compositions and structures of initial rocks are clearly fixed in metasomatites on particular extensions of dark-coloured minerals. Together with albites in subordinate quantities are often encountered microclines. In zones of transit from intervening rocks to albitites are highly usual alkaline amphiboles (arfvedsonites) and also relict minerals.

Quite often sodic metasomatism is superimposed on enclosing rocks undergoing keratinization and fenitization, which exert a substantial influence on composition and structure of metasomatites.

Albitization of nephelinic syenites is accompanied by addition of alkali and removal of alumina, potassium, calcium, iron (table 21.2). Sodium content does not substantially change. With albitization of quartz-containing rocks take place removal silica and addition of alumina and sodium.

Table 21.2. Change of chemical composition of nepheline syenites of Djilisuiskoe massf and aleurite slates at their albitization in weight % .

Compo- nents	1	2	3	4	5	6
SiO ₂	55,44	58,00	66,00	78,09	67,43	65,56
TiO ₂	0,38	0,20	0,07	0,62	0,69	0,65
Al ₂ O ₃	22,47	21,74	21,06	8,13	11,63	17,07
Fe ₂ O ₃	1,39	3,31	0,47	0,47	2,61	2,21
FeO	1,35	0,62	0,08	3,09	1,33	1,07
MnO	0,11	0,05	0,01	0,05	0,38	0,65
MgO	0,22	0,25	0,02	1,70	1,63	0,70
CaO	1,37	0,70	0,46	3,36	3,85	0,70
Na ₂ O	9,57	10,84	10,31	1,08	6,88	8,18
K ₂ O	5,37	3,05	0,33	1,46	1,12	1,95
H ₂ O ⁻	0,05	-	0,25	-	-	-
H ₂ O ⁺	0,49	0,08	-	0,04	0,04	0,16
Loss. fire	2,00	1,17	0,55	1,19	2,71	0,55
P ₂ O ₅	0,10	0,02	0,03	0,25	0,10	0,08
Nb ₂ O ₅	n.d	n.d	0,16	n.d	n.d	n.d.
Ta ₂ O ₅	n.d	n.d	0,02	n.d	n.d.	n.d.
Total	100,31	100,03	99,82	99,53	100,40	100,63

1 – nepheline syenite; 2 - albitized nepheline syenite; 3 - albitite on nepheline syenite; 4 – aleuritic slates; 5 - albitized hornfels on aleuritic slate; 6 - albitite on aleuritic slate. n.d. - element non determined; dash – content of element under the limit of detection

Horizontal metasomatic zoning in nephelinitic syenites appears indistinctly. The basic volume of albitized rocks is composed of transient varieties, in which are present relicts of nepheline, more or less mixed with albite. Albitites in which nepheline is not preserved, do not constitute more than 10% of the total volume of the metasomatic bodies. The study of sections selected on cuts across the strike of metasomatic bodies permits to outline the following scheme of the structure of metasomatic columns: Unchanging nephelinitic syenite → nepheline + microcline + albite + biotite → nepheline + microcline + albite + aegyrine → albite + nepheline + aegyrine → albite + aegyrine → albite. The ore minerals pyrochlore and zircon strictly coincide with zones of albitite-aegyrine and albite composition.

In much greater contrast appears the zoning in the zone of exocontact. The boundaries between zones are precisely and easily fixed in the process of documentation. The composition of outer and intermediate zones is strongly linked with the composition of initial rocks. The albitization process is often preceded by contact keratinization and fenitization; moreover, the deposit of each of these processes in the final composition and structure of the metasomatite cannot always be evaluated. Below is given as example a metasomatic column, arisen at the expense of keratinization of aleuritic schist: quartz + chlorite + biotite + sericite + calcite → quartz + actinolite + biotite + albite + calcite → quartz + albite + arfvedsonite + microcline + calcite → quartz + albite + arfvedsonite + microcline → albite + arfvedsonite + microcline → albite + aegyrine + microcline → quartz + albite + aegyrine → albite. Coincidence of ore minerals with determined zones in metasomatic zones of exocontact appears very clearly. So, thorite together with fluorite in the form of fine bi-pyramidal grains (tenth or hundredth fractions of mm) is formed in zones of stability of quartz with arfvedsonites and albites. In a quartz-albite-arfvedsonite-microclinitic zone thorite content reaches a maximum, and in the following albite- arfvedsonite-microclinitic zone is recorded its collective crystallization on a background of replacement by other minerals. Here thorite forms prismatic crystals with pyramidal ends measuring up to 5 mm. In thorite is present a great quantity of inclusion of albite, microcline, arfvedsonite and fluorite. In the albite-aegyrine-microclinitic zone, together with prismatic grains of thorite, is formed coarse xenomorph thorite (grain dimension up to 1 cm). Quantitatively the inclusion in thorite increases so significantly (up to 95%) that in essence we have to do with pseudomorphoses of rock-forming minerals on thorite. The thorite itself deposits like a skeleton, depending on the general peculiarity of the thorite's form of secretion. In the albite-aegyrine-microcline zone thorite is completely replaced by rock-forming minerals. Instead of thorite grains remains a reddish-brown patch, giving the possibility of judging preceding contours of the mineral. Thus, in a metasomatic column is established a new formation of thorite on outer zones, its crystallization with formation of

skeleton forms in the intermediate zones and completely replaced in the inner ones. It is obvious that thorite is indissolubly linked with the processes of formation of metasomatic columns, occupying in them a clear position. Pyrochlore forms tiny granules (of tenths of mm) characterized by a regular octahedric form, it is found in irregular accumulation and close grouping. It is recorded exclusively in inner zones of metasomatic bodies essentially of albitic and albite-aegyrine composition, independently of the initial composition of the rocks. We must emphasize that the described metasomatites are clear examples of contemporary processes of metasomatic rock transformation and ore deposition.

Metallogenetic and geochemical specialization. Under its predominant aspect of mineralization, is pyrochlore-zircon, concentrated in albitites. Thorite (ThSiO_4) is formed only in the albitization of rocks, enriched with silicic acid, which characterizes only metasomatites of zones of exocontact of nephelinitic syenitic massifs. Uranium under the aspect of isomorphic admixture exists in thorite, pyrochlore and other minerals. Of rare minerals characteristic of albitites there are monazite, orthite, aeschynite, chevkinite. E.M.Eskova [1976] has presented an extensive list of other minerals with high concentration of rare-metal and rare-earth elements.

Geochemical specialization of metasomatites is determined by increased temperature, alkaline character of the solutions and high sodium activity. So, as with the formation of sodic metasomatites of other genetic types, such conditions favour migration of titanium, silicon, phosphorus, zircon, thorium, niobium, tantalum, rare earths.

Conditions of formation. Temperature conditions of albitization, judging from available data, oscillate between 500 and 400°C. Oxidized form of iron in albitites (aegyrine present) testify not only to the high oxidizing-reducing potential but also to the high alkalinity of the solutions. The wide extension of albitized nephelinitic syenites with relicts of nepheline (mariupolites) proves that the process of rock formation of the zone of endocontact, basically, is hampered by the reaction of replacement of nepheline by albite. This is linked with the fact that a full replacement of nepheline by albite may occur on condition of removal of alumina, or of inert behaviour of alumina, on condition of increase of the metasomatite volume compared to the initial rocks. Realization of these conditions in nature is difficult. The change of nephelinitic syenites into albitites, basically, occurs at the expense of relatively thin dykes and apophyses. Transformation of quartz-containing enclosing rocks into albitites is produced on great scales. With this is recorded a clear metasomatic zoning, and on the whole volume of metasomatic bodies the albitites have a leading role. Albitite zones of exocontact in relative ore-content proves very productive.

21.3. Albitites, a family of low-temperature sodic metasomatites.

Definition. The first large development of periere albitization was recorded in an uranium deposit of Ace in the region of Beaverlodge Lake in Canada, where albitization is accompanied by formation of chlorite, carbonate and hematite [Dawson, 1951]. Later, this process was studied in detail in the uranium deposits of Kazakhstan [Omelyanenko, 1970; Omelyanenko & Lisitzyna, 1974], where it was proved that albitized rocks of that sort present themselves as specific formation types of periere metasomatites. One calls aceites metasomatic rocks mixed with uranium deposits, and deposits of albite, carbonate, hematite and chlorite.

Geological setting. To aceitization are subjected rocks of various form: granites, sandstones, limestones, basalts, gabbro etc. in hinge zones of basins, completed by sedimentary rocks, with upheavals. In northern Kazakhstan, where periere aceitization in uranium deposits is wide-spread, that process coincides with zones of fractures and takes place either in intrusive rocks or in sediments mixed with them. On the Manybaïskoe deposit aceitization is situated along the zone of the main north-eastern fault and the system of finer dislocations connected to them on a few kilometres and reaching to a depth of 1 km. The thickness of the metasomatic aureole reaches a few hundred metres. The N-E fault divides its aureoles in two parts: in the eastern one metasomatism is situated on the sedimentary rocks of the East-Kokchetavsk basin, and in the western on the quartz diorite Aksuisk massif.

The degree of transformation of the rocks varies and depends upon the intensity of their fracturation.

Mineral composition, facies and zoning of aceites. The main mineral of aceites is albite; carbonates and hematite are present as accessory minerals; chlorite and quartz are often present as intermediate products. In calcicium-enriched rocks, the chief role is played by uranium-containing fluorine-apatite, up to formation of uranium-bearing apatitic metasomatites on limestones [Omelyanenko *et.al.*, 1974]. There is characteristic

Table 21.3. Change of chemical composition of red- colored quartzitic sandstones in process of aceitization, % weight

Compo- nents	Unaltered sandstone	Aceitized quartzitic sandstones				
SiO ₂	77,08	73,62	76,02	74,22	57,00	42,30
TiO ₂	0,18	0,20	0,14	0,20	0,20	0,20
Al ₂ O ₃	12,10	11,35	11,65	11,59	17,89	13,43
Fe ₂ O ₃	1,95	0,74	-	0,52	1,50	8,84
FeO	0,29	0,24	0,58	0,13	0,21	0,30
MnO	0,01	0,01	0,01	0,01	0,04	-
MgO	0,04	0,08	0,21	0,05	0,31	-

CaO	0,43	3,42	2,46	2,40	5,01	12,30
Na ₂ O	4,60	4,50	5,09	6,31	8,37	6,05
K ₂ O	2,40	2,09	1,59	1,51	1,39	0,57
H ₂ O ⁻	-	-	-	0,51	1,92	0,53
H ₂ O ⁺	1,20	0,99	1,43	0,56	0,61	1,38
CO ₂	-	0,25	-	-	-	0,33
S	-	-	0,02	-	-	0,11
P ₂ O ₅	0,08	1,95	0,94	1,36	3,31	6,67
ZrO ₂	n.d.	n.d.	n.d.	n.d.	2,50	6,030
Total	100,36	99,44	100,14	99,37	100,26	99,31

Analyses performed in the Central laboratory of chemistry of Acad.Sc. of USSR by E.F. Kalachnikova

instability of quartz during aceitization, which is replaced by albite. In correspondence with the variation of mineral composition, determined, grosso modo, by the composition of enclosing rocks, are divided the facies of aceites: quartz-albite, calcite-albite, chlorite-albite, ankerite-albite, albite-apatite, apatite-albite and apatite.

Periveinous zoning in beresitized rock has usually the following structure. On granites: 0) granite (quartz, oligoclase, microcline, biotite, magnetite); 1) quartz, albite, sericite (on microcline), microcline, chlorite, calcite, hematite; 2) quartz, albite, chlorite, calcite, hematite; 3) albite, ankerite (or chlorite), hematite; 4) albite, hematite. On diorites: 0) diorite (ankerite, hornblende, magnetite); 1) albite, chlorite, calcite, sericite, hematite; 2) albite, chlorite, calcite, hematite; 3) albite, ankerite (or chlorite), hematite; 4) albite, hematite. In external and middle zones occur minerals which disappear to the extent of the growth of intensity of the process into the inner zone (sericite, chlorite).

Chemism of the aceitization process. Upon aceitization are added sodium and carbon dioxide, in certain cases phosphory, partly calcicium. There is removal of potassium, silica and magnesium. The tendency to change of chemical composition of rocks with aceitization is shown on table 21.3. The behaviour of alumina is multiform, though, on the whole, it is little mobile and, as a rule, it is not added (albite is formed only on alumina-bearing rocks). With exchange of interstratified argillites, aleurolites and sandstones there occurs local mixing of alumina with its removal from argillites and addition in sandstones. Judging from the forming parageneses of minerals, aceitization is a typical alkaline process, parageneses produced by hydrocarbonate-sodic solutions with low activity of sulfide sulphur and high activity of oxygen. One notices a high mobility of titanium, phosphory, zirconium and silica.

Aceitization and ore deposition. Aceites are distinctly specialized on uranium. This is a clear type of metasomatites, which is almost never found without uranium mineralization and does not carry industrial concentration of

practically any other metals. In a few uranium deposits are found portions with molybdenum and zircon ore, but these ores have the character of accompanying the uranium.

The evolution of metasomatic-uranium-ore processes is reflected in the succession of actinization, apatitization, carbonatization, ore deposition with chloritization, post-ore veins and veinlets. The basic mass of hematite is accompanied at the beginning of an ore stage and is deposited together with an apatite-arshinovite association on the inner zones of columns of peri-ore actinization. In some cases, intensive hematitization is accompanied with addition of iron. Following this association ankerite is deposited in the form of veinlets and metasomatic accumulation. An ore stage is completed by formation of micro-veinlets and accumulation of pyrite, pitchblende, molybdenite and coffinite, which are accompanied with “ore” chlorites. The post-ore stage presents sparse veins and veinlets of quartz, chlorite, baryte, calcite, fluorite and pyrite.

CHAPTER 22

Gumbeites

Definition. Gumbeitized rocks were distinguished by D.S. Korzhinsky [1948] as products of an independent metasomatic process in the Gumbeyka basin in southern Ural. This is a periveinous alteration of granodiorites with distinct manifestation of lateral zoning. Strictly, the rocks called gumbeites occupy an inner zone in a column of gumbeitization and consist in the typical case of quartz, orthoclase and carbonate. Usually there exist in them ore minerals of sulfides and scheelite. In the outer zone of gumbeitized rocks are characteristically present phlogopite or slightly ferrous biotite. Intrusive massifs containing quartz veins with fringes of gumbeitization are composed of alkaline granodiorites and varieties transient to syenites. In contact with a volcanic mass of diabasic porphyrites they are replaced by syenite-diorites. Quartz veins outside the intrusive massif are accompanied by beresitization, but there is no potash .feldspathization

Gumbeites of the Gumbeika deposit of scheelite. Gumbeites of the Gumbeika deposit of scheelite [Spiridonov et al.,1997] have replaced monzonites quartz syenodiorites, syenite-porphyry and serpentinites, but also hornfelses, biotite-amphibole metasomatites and propylites. The gumbeite margins are 3-10 cm thick, rarely up to 50 cm. The thickest margins develop on biotite-amphibole rocks and serpentinites.

Two types of quartz veins and the gumbeites accompanying them are distinguished: earlier ones, formed of dark-grey quartz with admixture of biotite, potassic feldspar and molybdenoscheelite, with biotite-potassic feldspar vuggy fringes in selvages, and the later ones, formed of bright quartz with admixture of carbonates, potassic feldspars, scheelite, more rarely molybdenic scheelite, sulfides, with carbonate-potassic feldspars vuggy fringes in selvages. A succession of vein formations is established on their intersection. In gumbeites with a biotite-potassic feldspar rear zone develops molybdenoscheelite; in gumbeites with a dolomite-feldspar zone develops scheelite. Possibly scheelite has developed simultaneously with the usual gumbeites, or has been replaced by

molybdscheelite. Starting from these mutual reactions one may surmise that the usual gumbesites form later than these with a biotite-feldspars-quartzic rear zone.

The typical zoning of early gumbesites with biotite-orthoclase (or microcline) rear zone:

Zone 0. Unaltered quartz-syeno-diorite: hornblende (10-15%), biotite (5-10%), micro perthite (40-50%), plagioclase An 20-25(15-20%), quartz (5-10%); accessory: titanomagnetite, sphene, apatite.

Zone 1. biotite (20-30%), calcite (10-15%), albite(15-20%), quartz (up to 10%), orthoclase (microcline) (40-45%), pyrite, sphene, apatite, sometimes monazite. Biotite ferruginosity amounts to 35-40%, Al content = 1-1,2 formula unit.,TiO₂ up to 2,5 weight. %.

Zone 2. biotite (20-30%), calcite (10-15%), quartz (up to 10%), orthoclase (microcline) (50-60%), pyrite, sphene, apatite. Quite often in orthoclase grains is preserved relict albite. The thickness of this zone does not exceed 2-3 mm.

Zone 3, borders upon quartz vein: biotite (20-40%), orthoclase (microcline) (up to 70%), quartz (up to 10%), pyrite, apatite, rutile. The zone is 3-5 mm thick.

Zone 4, a rear-zone: quartz-vein with molybdscheelite, biotite, rutile, sometimes potassic feldspar. Molybdscheelite has formed simultaneously with other minerals of metasomatites, as far as it forms the boundary of joint growth with biotite.

At the transition from granitoids to a quartz vein on the boundary zone there occurs the following reaction of replacement :

0 zone → 1 zone: $Hb_1 = Cc + Bi + Py$; $Olg = Ab + Cc$; $Ti-Mt = Py + Spn$.

1 zone → 2 zone: $Ab = Mc$.

2 zone → 3 zone: $Spn = Rt$, Cc dissolves.

The zoning of late gumbesites with carbonate-feldspar rear zone is distinguished by the development of dolomite instead of calcite.

Zone 0.unaltered quartzic syeno-diorites: hornblende (10-15%), biotite (5-10%), microperthite (40-50%), plagioclase an 20-25 (15-20%), quartz (5-10%), accessory metals: titanomagnetite, sphene, apatite.

Zone 1: sericite (15-20%), biotite (up to 2-5%), dolomite (20-25%), potassic feldspar (30-40%), albite(15-20%), quartz (up to 10%), pyrite, sphene. Biotite ferruginosity 35-40%. Sericite is usually represented by phengite or is close to it. Dolomite ferruginosity amounts to 10%. The zone thickness is from 3,5 cm to 10 cm.

Zone 2: dolomite (20-25%), potassic feldspar (up to 40-50%), biotite (2-5%), albite (15-20%), quartz (up to 5%), pyrite, sphene, apatite. The thickness is 0,5-1 mm.

Zone 3: dolomite (20-25%), potassic feldspar (up to 70%), biotite (up to 5%), quartz (up to 5%), pyrite, sphene, apatite. In orthoclase grains is found relict albite. The thickness is 0,5-1 mm.

Zone 4: enjoining a quartz-vein: drusic crust of orthoclase (70-80%) with dolomite (20-25%), quartz (up to 5%), pyrite (up to 5%), rutile and apatite. The thickness is 2-3 mm, up to 1cm.

Zone 5, a rear zone: quartz vein with scheelite, dolomite, orthoclase, rutile. Scheelite forms simultaneously with other minerals of metasomatites.

On transformation from unaltered rocks to quartz veins on the boundary zones occur the following reactions of replacement:

0 zone → 1 zone: $Hb_1 = Dol + Ser + Bi + Py$; $Bi_{relict} = Ser + Dol + Py$;

$Olg = Ab$; $Ti-Mt = Py + Spn$.

1 zone → 2 zone: $Ser + Qtz = Mc$.

2 zone → 3 zone: $Ab = Mc$.

3 zone → 4 zone: $Spn = Rt$; $Bi = Dol$.

Chemical composition as gumbaites in initial rocks is given in table 22.1.

Table 22.1 Chemical composition of protolithes (1) and gumbaites (2) (% weight)

Compo- nents	A ₁	A ₂	B ₁	B ₂	C ₁	C ₂
SiO ₂	51,70	45,30	44,68	28,64	38,47	36,03
TiO ₂	0,83	0,84	0,71	0,64	2,98	2,79
P ₂ O ₅	0,70	0,51	-	-	0,56	4,14
Al ₂ O ₃	14,72	13,47	11,49	8,87	14,02	13,48
Fe ₂ O ₃	2,32	1,19	7,90	5,28	10,98	4,32
FeO	5,20	5,14	7,15	3,57	2,86	7,88
FeS ₂	0,19	0,36	0,86	11,82	0,67	0,84
MnO	0,09	0,09	0,17	0,15	0,25	0,28
MgO	7,24	6,14	9,60	6,84	3,45	3,68
CaO	6,74	6,60	10,64	11,68	20,63	16,99
Na ₂ O	3,45	2,23	2,29	1,60	1,15	1,65
K ₂ O	3,24	3,72	2,47	4,62	1,51	3,87
H ₂ O ⁺	1,70	1,64	1,26	1,26	2,17	1,69
CO ₂	1,64	12,30	1,16	15,70	0,58	2,80
Total	99,76	99,53	100,38	100,67	100,28	100,44
density gram/cm ₃	2,86	2,84	-	-	3,35	3,35

Note: A-C - Gumbeika ore field, D-F - Shartash ore manifestation.

Protolithes: A₁ - monzonites, B₁ - oligoclase-biotite-amphibolic rocks, C₁ – amphibolized rodingites, D₁, E₁ - adamellites, F₁ - microadamellites.

Gumbaites: A₂ - dolomite-biotitic, B₂ - calcite-dolomite-biotitic, C₂, D₂ - dolomitic, E₂, F₂ - phengitic.

A, B - data of D.S. Korzhinsky; D, E – data of A.I. Grabezhev; C, F – data of E.M. Spiridonov *et al.* [1997]. Quantitatively calculated pyrite on quantitative sulfur, respectively Fe₂O₃ content corrected in analyses.

Table 22.1 continuation

Compo- nents	D ₁	D ₂	E ₁	E ₂	F ₁	F ₂
SiO ₂	72,48	70,82	70,12	65,00	67,45	62,99
TiO ₂	0,24	0,18	0,28	0,30	0,46	0,47
P ₂ O ₅	-	-	0,10	1,51	0,25	0,18
Al ₂ O ₃	15,00	14,52	15,08	15,66	15,78	15,67
Fe ₂ O ₃	0,26	0,21	0,92	1,01	2,17	0,11
FeO	2,47	1,41	2,10	0,64	1,19	0,87
FeS ₂	traces	0,66	-	1,93	traces	3,80
MnO	0,04	0,03	0,04	0,05	0,12	0,11
MgO	0,10	0,20	0,93	0,60	1,44	1,57
CaO	1,65	1,71	2,14	2,72	2,79	2,78
Na ₂ O	4,26	2,40	5,22	1,60	4,87	0,34
K ₂ O	2,76	4,82	3,18	6,18	2,96	7,89
H ₂ O ⁺	-	2,05	0,18	4,10	1,22	1,55
CO ₂	traces	0,65	-	-	0,18	2,03
Total	99,26	99,66	100,29	101,30	100,88	100,45

For metasomatites on serpentinites is established addition of silica in rear zones (outer zones are unsaturated with silica, in rear zones occur quartz-containing parageneses. The ore mineral in these metasomatites is represented by pyrrhotite, not by pyrite.

Zone 0: immobile serpentinite.

Zone 1: magnetite, talc, dolomite, phlogopite, pyrrhotite.

Zone 2 (rear) : phlogopite, talc, dolomite, quartz, pyrrhotite.

In the Gumbeika deposits it is possible to distinguish at least three degrees of temperature of metasomatites and of the quartz veins linked with them.

1. Gumbeites with rear biotite-feldspar-quartz zone and associations biotite+calcite+quartz+feldspar in intermediate zones. With these gumbeites are linked veins with molybdoscheelite, forming at 400-400°C (according to data of study of individual gas-liquid inclusions in quartz and molybdoscheelite [Spiridonov *et al.*, 1997].

2. Gumbeites with rear dolomite-feldspar-quartz zone and association of dolomite + biotite + feldspar + quartz or dolomite + calcite + feldspar + quartz in

intermediate zones. With these are linked quartz veins with molybdoscheelites, formed at 395-360°C [Spiridonov *et al.*, 1997].

3. Gumbeites with rear dolomite-feldspar-quartzic zone and association of dolomite+biolite+feldspar+quartz or dolomite+calcite+feldspar+quartz in intermediate zones of the column. To them are contiguous quartz veins with scheelite and sulfides, formed at 350-290°C [Spiridonov *et al.*, 1997].

Analysis of parageneses of gumbeitized rocks has established the following series of mobility:

H₂O, CO₂, S, O | K₂O, Na₂O, CaO | MgO | Fe, SiO₂, P₂O₅, Al₂O₃, TiO₂.

The first line distinguishes elements which on gumbeitization always behave in complete mobility; the second line distinguishes elements moving in the rear zone, correspondingly, the more to the left is an element in the series of mobilities, the earlier it passes to a complete mobility; the third one distinguishes elements with a thermodynamic mobility only observed for metasomatites with a quartz-biotite-feldspar rear zone, i.e. at the highest temperatures; to the right of the third line are elements always inert. For elements rich in calcium and poor in magnesium, the series of mobilities somewhat changes:

H₂O, CO₂, S, O | K₂O, Na₂O, MgO | CaO, Fe, SiO₂, P₂O₅, Al₂O₃, TiO₂.

With gumbeitization is added first of all carbon dioxide, i.e. basically this is carbonatization. Furthermore, addition is observed of sulphur, potassium, and removal of sodium.

In rear zones of metasomatites is usually observed an increase of phosphory content (accumulation of apatite), tungsten (scheelite and W-containing rutile), often increase of silica content (particularly with gumbeitization of serpentines). The quantity of apatite usually decreases compared to that of scheelite: their richest accumulation is in nests amidst marbles. Active migration of complex-forming elements (phosphory, tungsten and silica) may be linked with infiltration of solutions along central fractures, so that mineral composition of ore veins gets subordinated to the rules of infiltration metasomatism. Zoning of periere gumbeites is formed with diffusion metasomatism and is characterized by the small thickness of metasomatic zones.

In the Gumbeika deposit is established an exchange, habitual to postmagmatic hydrothermal deposits, of high temperature mineral associations with low temperature ones: molybdoscheelite is replaced by molybdenum-bearing scheelite and scheelite, tennantite is replaced by tetrahedrite (tennantite is a faded ore hotter than tetrahedrite). Presence of molybdoscheelite, hematite, Cu²⁺ and Te in the composition of faded ores testify to increased oxidizing potential, condition of mineral-forming gumbeitic formation. At low temperature occurs a lowering of oxidizing potential: molybdenite (Mo⁶⁺) is replaced by scheelite with molybdenite (Mo⁴⁺), tellurium containing faded ores

(Te^{4+}) by tellurides (Te^{2+}), and the quantity of Cu^{2+} in the composition of faded ores also diminishes.

Gumbeites of the Shartash scheelite ore deposit (Berezovskoe auriferous field). The Shartash tonalite-granodiorite intrusive is situated in the southern part of the Berezovo auriferous field. Its formation was assured by that of post-magmatic hydrothermal metasomatites in succession from early to late: 1) quartz muscovite with quartz-turmaline veins, 2) quartz sericite metasomatites with Cu-Mo-mineralization, 3) propylites with orthites, 4) gumbeites (stockworks and periveinous) with scheelite mineralization, 5) beresite-listwaenites with gold mineralization, 6) argillisites.

Metasomatites of gumbeite family the Shartash massif is composed of symmetrical fringes around abruptly dipping quartz and carbonate-quartz veins. Fringe thickness is usually 10-20 cm, rarely up to 1 m.

Two types of quartz veins and gumbeites accompanying them are distinguished: an earlier one, composed of cream-white quartz with admixture of dolomite (or calcite), feldspar, scheelite, molybdenite and other sulfides, with dolomite-microcline (more rarely calcite-microcline) vuggy fringes, and a later one, composed of carbonates and quartz with admixture of scheelite and sulfide, with carbonate (dolomite or calcite)-sericite-microcline vuggy fringes. The first type of veins is linked with gumbeites of dolomite-feldspar facies. The second type of veins is linked with a low temperature microcline-phengite facies of gumbeites.

General lines of gumbeite formation in Ural. On the considered material of gumbeites and the quartz veins linked with them it is possible to distinguish three facies according to the temperature of the formation:

1. Biotite-potash feldspar facies. It is accompanied with biotite quartz veins with pyrites and molybdenoscheelite. Temperature of its formation is 440-400°C.

2. Dolomite-potash feldspar facies. It is accompanied with carbonate-quartz veins with Mo-scheelite, scheelite, molybdenite, bismuthite, galenite, aikinite, tetradymite, faded ores. In the quartz veins of the Shartash ore display, are established, linked with this facies of gumbeites, solid solutions of aikinite-bismuthite and Cu-benjaminite-cupropavonite series. Temperature of gumbeite formation, 400-300°C; the ore minerals formed at 400-200°C.

3. Phengite-potash feldspar facies. It is accompanied by carbonate-quartz veins with sphalerite, galenite, tetrahedrite, bournonite, tetradymite, hessite, gold. Temperature : 300°C.

The most extended facies of gumbeites is the dolomite-potash feldspar (found in all the considered uranium deposits). A higher temperature biotite-potash feldspar facies is established at present only on the Gumbeika deposit. Low temperature phengite-potash feldspar facies is widely spread only in the Shartash ore display.

The principal significance for the formation of gumbaites belongs to high potassium activity, leading to the appearance of a steady paragenesis of quartz + potash feldspar + carbonate under fully mobile behaviour of potassium. Established is also a high oxidizing potential, with formation of molybdenoscheelite, hematite, cupreous and telluric faded ores. At the end of the process potassium activity apparently decreases (display of potash feldspar-phengite facies of gumbaites); at the same time the oxidizing potential also decreases (with the potash feldspar-phengite facies are connected faded ores, containing no Cu^{2+}).

Gumbaites of gold-ore deposits. Gumbaites in gold-ore deposits are formed at lower temperature than in displays of mineralization of tungsten and molybdenum, and are distinguished by mineral associations. Examples of gold ore gumbaites were described by I.P. Shcherban [1996] for the Zarmitan deposit in west Uzbekistan. The zoning of such periveinous gumbaites, substituting granosyenites, according to his data, has several aspects: 1) unaltered granosyenite (potash feldspar + plagioclase + quartz + hornblende + biotite); 2) altering granosyenite (potash feldspar + plagioclase + quartz + chlorite + sericite + carbonate); 3) potash feldspar + plagioclase + albite + carbonate + quartz + sulfides; 4) potash feldspar + albite + quartz + sulfides + carbonate. The difference from tungsten gumbaites of the Ural consists in the absence of phlogopite on the outer zones of the gumbait column. I.P.Shcherban links the absence of phlogopite with the lower temperature of metasomatism, at which instead of phlogopite appears chlorite. In the Zarmitan deposits are distinguished 5 stages of mineralization: quartz (350-500°C), gold-pyrite-arsenopyrite (230-350°C), galenite-sphalerite (130-330°C), sulfosalts (100-150°C) and low temperature carbonate. Gumbaitization was accompanied by a second stage (gold-pyrite-arsenopyrite) and was produced between 250 and 350°C, with corresponding middle temperature process. Other differences consist in the correspondence of two feldspars in the inner zone of the gumbait column. In the presence of quartz this testifies to the inert behaviour either of potassium or of sodium, which may be linked with increased alkalinity of the milieu and be a consequence of increased alkaline activity. The presence of sericite in the zoning, is most probably the result of extended combining of parageneses at different times, since paragenesis of quartz with both feldspars and sericite does not occur in nature.

In described gold-bearing gumbaites the potash feldspar contains a noticeable quantity of sodium, judging by the extension of perthitic ingrowths in them. From the description it is not clear whether they are relicts (from feldspar in granosyenite) or linked with increased sodium activity at gumbaitization.

Thus, gumbaites present themselves as the result of metasomatism of granitoids (more rarely of volcanic rocks), of high alkalinity under the influence of solutions presenting high activity of alkalis, principally

potassium. Temperature of the process, according to the available estimations, strongly varies from zero to 400°C. The composition of the solutions forming gumbeites has not been determined, but according to indirect data these solutions, apparently, were fluor enriched. This is testified by data of experimenting on forms of transfer of tungsten and molybdenum in hydrothermal solutions, and also data of research on fluid inclusions in the minerals of tungsten-bearing veins. Gumbeites are typical periveinous formations and develop around quartz-carbonate-orthoclase veins in ore mineralization of tungsten, molybdenum and gold.

CHAPTER 23

Argillisites and argillised rocks

Definition of the family. The term, designating the replacement of initial rocks by argillaceous minerals and invented in the second half of the 19th century, began to be widely employed in the geological literature in the forties of the 20th, especially after the revelation in connection with these metasomatites of deposits of various useful minerals. A substantial contribution to the description of the argillization process was made by T.S.Lavring, the first to utilize this term to designate argillaceous alteration of enclosing rocks near ore veins. To the further question of petrology and the geological aspects of argillization was devoted a vast literature [B.Schwarz, R.Sales, S.Meyer, N.I.Nakovnik, S.I.Nabokov, & *al.*]. The history of the origin and modification of the notions of “argillization” and “argillisites” has been minutely investigated by G.T.Volostnykh [1972]. According to him, argillization must be counted amidst metasomatic hydrothermal processes occurring at more than 50°C, and is expressed in the replacement of rocks by argillaceous minerals.

Argillisites are reliably known, starting with late Paleozoic, and their maximum development occurred in Mesozoic and Cenozoic times. Unlike the other metasomatic formations, argillisites extend practically to all geotectonic structure both of the oceanic and continental crust.

Geological setting. Argillised rocks occupy local zones in crystalline rocks; linear and complex stockwerk bodies in effusive and extrusive facies of volcanites occupy an enormous area in the stratified permeable effusive-sedimentary stratas. Mineral transformation is traced to the depth of the order of 1,5 km under the contemporary surface; moreover, feeble displays of argillization may be observed at greater depth.

Argillization may be associated with magmatites of various composition or they have no link at all with magmatic events (for instance, bentonites and a few other various argillisites in sedimentary-effusive stratas and platform area).

Direct links between argillisites and magmatic events take place only in the limits of volcanic fields. Portions of unloadings of thermal waters, accompanied with large alteration of subneutral type (Pauzhetka, Wairakei, etc.) usually do not coincide with concrete volcanic activity, but are localized in fracture zones controlling volcanic activity.

Table 23.1. Geotectonic frame and mineralizations of main facies of argillisites

Geotectonic position					Mineralization
Fractures of oceanic crust	Island arcs and continental margins	Areas of Intracontinental activation	Platforms		
-	Smectite-Zeolitic (Severnoie)	Kaolinite-smectite, smectite-zeolitic, carbonate-kaolinitic (Marysvale, Mogotcha, Olov)	A kaolinite-smectite (Adamovka)	U	
-	Quartz-alunite-kaolinitic (Karamken)	Quartz-illite-smectitic (Balei)	-	Ag, Au	
-	Quartz-hydromica-kaolinitic	-	A quartz-tossoudite-kaolinite (Nikitovka)	Hg, As, Sb	
Opal-smectitic (Kuriles)	Quartz-smectite-hydromicaceous (pyritic deposits of uranium type and type of kuroko)			Zn, Cu	
Smectite-celadonitic	Opal-kaolinitic, solfatara-smectite-zeolitic of thermal fields	Smectite-zeolitic (deposits of bentonites and zeolites)	? Smectitic (bentonites)	Non-metallic or ore-free facies	

Argillization is usually compared with superficial stages of development of geological processes, one nearly always younger than the latest magmatic transformations, and displays of higher-temperature metasomatism. The argillization process includes two branches: the hydrothermal argillization, accompanied by ore mineralization, and the solfatara one, as a rule oreless, coinciding with volcanic edifices [Korzhinsky, 1953; Zharikov & Omelianenko, 1965]. Their distinctions are linked with peculiarities of geological-structural conditions of localization and acidity of the influencing solutions. So, the first ones most often coincide with steeply falling fracture zones and are influenced by slightly acid solutions, and the second may have a regional extension and be conditioned either by sulfatic or by sulfato-chloridic solutions. Table 23.1 illustrates the dependence of the various phases of development upon their geotectonic situation and the coincidence of mineralization with determined metasomatic facies. It is evident that most potentially ore-bearing are argillites of continental margins and areas of superimposed intracontinental activation. Mineral composition.

Smectites represent the most wide-spread group of minerals in all the various argillites, except the most acid facies. The composition of hydrothermal smectites corresponds, grosso modo, to strictly montmorillonites and beidellites, but nontronites and saponites are sometimes found only in basic alterites. This property noticeably distinguishes smectites of hydrothermal genesis from hypogenesis. On the whole, in hydrothermal smectites either of montmorillonitic or beidellitic composition, the content of Mg and Fe in the octahedrons does not exceed 0,5-0,6 f.u. already at their substitution to rocks of basic composition, which is seen on fig.23.1, where the field of hydrothermal smectites is distinctly outlined. The iron's high acidity is characterized in this way: usually the $Fe^{+3}/Fe^{+2}+Fe^{+3}$ ratio is not less than 0,9. High-magnesian smectites such as the so-called "even-type"(cheto) and the trioctahedric saponite have a sedimentary genesis [Drits & Kossovskaja, 1990]. In connection with the limited iron and magnesium content of the octahedric coordination the hydrothermal smectites are similar to metasomatic micas of beresites and hydromicaceous metasomatites, in which the total Mg+Fe content also does not exceed 0.5 fu. Trioctahedric saponites are rare enough in the periphery aureoles of argillization in basic rocks and in much greater extension in meteoric alteration crusts and sedimentary series. The value of the total layered charge of smectites may vary from 0.23 to 0.65, and in the composition of interlayer cations Na and Ca usually predominate over subordinate values of K and Mg. Si and Al isomorphism in tetrahedres is limited: moreover, tetrahedric Al content oscillates from a few percent in montmorillonites to 0.3-0.5 in beidellites; consequently, the layered charge may be concentrated not only in octahedres but also in tetrahedres. Highly charged smectites whose the charge of the layer is displaced to the tetrahedres, display a much more greater tendency to an

irreversible compression; therefore mixed-layered mica smectite minerals form readily [Howard & Roy, 1983; Drits & Kossovskaja, 1990; Sato *et al.*, 1996]. Highly charged smectites are particularly characteristic of perire rocks of epithermal deposits in volcanic stratas. From experimental works, but also from observed hydrothermal systems of contemporary volcanos [Eroshchev-Shak *et al.*, 1985, 1996; Howard-Roy, 1985; Malla & Douglas, 1987; Sato *et al.*, 1996] it follows that high-charge smectites may be indicators of higher-temperature condition than of low-temperature ones. Therefore a complementary charge is established through replacement of part of silicon by aluminium in the tetrahedres, which must be accompanied by partial structural reconstruction. With further growth of temperature (150° and more) high-charge smectites turn into mixed-micaceous minerals of the mica-smectite type.

Kaolinite mineral group of such wide extension. They represent, grosso modo, kaolinites and dickites, sometimes as halloysites and, rarely, nacrites. Kaolinite exists under two morphological aspects, as metasomatic thin-scaled aggregates replacing feldspars and dark-colored minerals and, more rarely, as filling of intersecting veinlets and zones of crushing. In the latter case may be observed relatively coarse-flaked aggregates and wormlike growths. The degree of crystallization of both varieties in perire argillites is usually high (Hinckley index about 0.6-0.8). In acid conditions (solfatara argillites) is often observed kaolinite with low degree of ordening (Hinckley index about 0.3) and halloysite.

Structural investigations [Eroshchev-Shak *et al.*, 1996] reveal a heterogeneous structure of hydrothermal minerals of the kaolinite group. It is conditioned by the appearance of irregular dickite-kaolinite mixed-layered phases (they usually contain not more than 5-10% of dickite-like layers). Apparently this 120°C temperature approximately corresponds to the limit of the domain of kaolinite-dickite synthesis. Dickites in ore deposits either form metasomatic secretions or fill cavities and fractures. Nacrite is observed only in intergrowths with ore minerals in epithermal gold-silver deposits.

Amidst *mixed-layered minerals* predominate illite-smectites, but one may also find chlorite-smectites, celadonite-smectites, kaolinite-smectites (the latter studied only in ultra-acid facies of argillization). Illite-smectites are found in all facies of argillization, usually in their outer and intermediate zones. Practically all mixed-layered mica-smectitic minerals are related to a particular potassium type, but sodium-containing paragonite-smectites (brammalites) are rare. This totally corresponds with the narrow range of variation of the K/Na ratio, with which may, in conditions of low temperature, co-exist sodium-containing micas and mixed-layered paragonite-smectites. Starting from data concerning the miscibility in the order of K/Na of dioctahedric mica [Popov, 1975; Iiyama, 1964], such minerals are established only in sodic milieu.

Hydrothermal mixed-layered illite-smectites contain 30% and more mica layers and are nearly exclusively characterized by factors of neighbouring order $S > 1$: $S=0$ in case of fully inordinate alternation of layers of micaceous and smectitic type; $S=1$ when the position of arbitrary layers in the crystal depends on one layer preceding it; $S=2$ upon two preceding layers and so on; in foreign literature the factor of neighbouring order is designated by the symbol R or g [Dritz & Sakharov, 1976].

The structure of these minerals strives to reach the maximum of possible degree of order, which is reflected in the predominance of layers of the type BA^nB (A is a layer of illitic type) [Dritz & Kossovskaya, 1990]. In argillites are most often found mixed-layered facies with 50-70% micaceous layers. Absence in hydrothermal metasomatites of mixed-layered illite-smectites with more than 50% content of swelling inter-layers and factor $S=0$ represents one of the characteristic properties of hydrothermal mineral formations. This phenomenon is noted not only for perire metasomatites [Diakonov & Volostnykh, 1979], but also for many contemporary thermal manifestation [Steiner, 1977]. Kinetics of illitization of smectites has been studied in enough detail and this has shown that the mechanism of transfer of smectite to illite in hydrothermal conditions substantially depends upon what takes place at the epigenesis of sediments. Experimentally determined energy [Eberl & Hower, 1976] of activation of this transfer at 260-390°C temperature, proving to be equal: $E=19,6$ Kcal/mol (83Kj/mol). Actually it coincides with the theoretically calculated one, coming from the energy of breaking of crystal bond and structural reformation the value of which must not be less than 80-100 kJ/mol [Velde & Vasseur, 1992]. For diagenesis conditions this value is estimated by the authors at 37-70 KJ/mol. The latter is rather characteristic of many exchange without destruction and reformation of tetrahedral layers, which is apparently less characteristic of hydrothermal conditions.

PH growth, preventing dissolution of initial smectite and decreased Al^{+3} activity increases the activation energy of transfer to 30 kcal/mol (~ 120 KJ/mol) [Robertson & Lahann, 1981]. This circumstance may partly explain the wide extension of hydromica and mixed-layered mica-smectites, specially in aureoles of acid leaching, but of smectites in subneutral conditions.

Increase of content of illitic interfoliated in mixed-layered mica-smectites from perire hydrothermal metasomatites is accompanied with a structural restructuration in the hexagonal grids of the layers 2:1, increased content of illite-layers and increase of concentration of layers with vacant transitions [Dritz et. Al., 1966]. This structural peculiarity of hydrothermal illite-smectites distinguishes them from diagenetic ones, which form without noticeable structure reformation, basically through solid phase reactions.

In low temperature hydrothermal argillization of some gold, uranium/mercury deposits in association with kaolinites is often found tossudite,

a di-trioctahedric mixed-layered mineral of the smectic-donbassite type with factors of neighbouring order $S=1$. Lithium comes in compositions of octahedric layers [Phineko *et al.*, 1977] but its content may exceed 1 mas.%. chlorite-smectites (corrensites) are relatively scarce and are found in altering basaltoids, some of which are basalts of the ocean bottom.

Celadonite belongs to a number of low-temperature minerals. It is recorded in argillized basalts or volcanoclastites of basic rocks on many uranium, gold, fluorite deposits; moreover it appears one of the main mineral apobasaltic argillisites of the ocean bottom. Undoubtedly the formation of this mineral promotes iron enrichment of the strata as well as the oxidity character of hydrothermal mineral formation in near-surface conditions at low temperatures (not more than 120-140°C). The degree of iron oxidation in celadonites from hydrothermal deposits from hydrothermal deposits and oceanic basalts is very high, the $\text{Fe}^{+3}/\text{Fe}^{\text{tot.}}$ ratio is 0.7-1. Potassium content oscillates from 4 to 8.5 mas.%, mingled-layeredness is more expressed in oceanic basalts, and the content of smectite mid-layers approaches 50%; moreover the factor of neighbouring order is $S>1$, which proves to be one of the differences of hydrothermal celadonites from sedimentary glauconites [Pritz & Kossovskaya, 1990]. Electronograms of celadonites, as a rule, contain clear enough reflexes on first and second ellipse, corresponding to the polytype 1M.

Zeolites represent the very characteristic group of minerals for some various argillisites. Amidst these are known low-silicic: laumontite, chabazite, as well as high-silicic: mordenite, clinoptilolite. The latter develop nearly exclusively on volcanoclastic rocks of acid composition and follow in significant degree the initial composition of the substratum. So, in zeolitic deposits of the Transbaikal region predominate potassic and sodic-potassic clinoptilolites and mordenites [Korobov, 1988], which apparently reflects the potassic character of the volcanites of this region. On the other hand, these high-silicic zeolites prove to be indicators of low-temperature conditions of mineralisation (~130°C and lower). Low-temperature zeolites in volcanites are much more rare and coincide with flows of basic lavas or with the horizons of their volcanoclastites. Amidst them are observed chabazite, desmine, faujasite harmotome, but this gathering of minerals, of course, is not conditioned by their temperature conditions but by the properties of the substratum composition. They are significantly absent in periore metasomatites as well as in veinous secretions of wairakite, which is widely spread in altering rocks of contemporary thermodisplays of the domain of active volcanism. It is known as the highest temperature zeolites and may be stable up to the ~290°C isotherm, which already exceeds the temperature condition of argillization. With periore hydrothermal metasomatism in the same temperature conditions develop instead carbonates in paragenesis with sericite (or other micaceous silicates).

Carbonates develop in these argillisites, which form in subneutral or feebly acid milieu. Metasomatic carbonates are represented, grosso modo, by ferrous dolomites, paraankerites, ankerites, siderites, magnesiosiderites. Calcites and dolomites are usually observed in intersecting veinlets and do not belong to substantially argillitic parageneses. On the whole, argillisites with participation in them of multiform ferrous carbonates are very characteristic of uranium deposits, reflecting to some extent specific ore-forming processes, in a given case of high activity of carbon dioxide and of the subordinate role of sulphur.

Alunite is typical of ultraacid facies of hydrothermal and synvolcanic argillisites. It has chiefly a potassic and potasso-sodic composition; sodic varieties are found very rarely. A high iron content, up to formation of jarosite, is noticed in alunites, forming on the surface or in zones of intense aeration of subterranean waters. Contents of potassium and corresponding K and Na in the composition of alunites from argillized rocks are indicated on the diagram, fig.23.2. Crystals of alunite of surface or near-surface genesis are strongly stretched along the crystallographic axis and have the aspect of spindles and needles. The temperature of their formation usually does not exceed 100-150°C. Higher temperature alunite from hydrothermal veins forms short-columnar crystals. Different morphologies are conditioned by disequilibrated growths in the first case and near-equilibrated ones in the second.

Chemical composition. Changes of chemical composition of rocks at argillization have their own properties in dependence upon conditions of the flow of the hydrothermal process. The basic tendencies of removal and redistribution of components in kaolinite-carbonate, kaolinite-smectite quartz-kaolinite argillisites, on the whole, are close and express lines characteristic of processes of acid leaching in general. Thus, in kaolinite-smectite facies is observed a distinct removal of alkaline earths and sodium, and in lesser degree of potassium. Noted are tendencies in various directions in the behaviour of alumina and silica, and an increased content of alumina linked with the massive development of clayed minerals replacing plagioclases, coloured minerals and potassic feldspars. In quartz-kaolinite facies decreased silica content in intermediate zones usually gives way to its increase in the inner one, linked with the development in many cases of quartz core. All divergences in the composition of alkaline-earth elements are linked with a more or less expressed carbonatization, but some increase of potassium in inner zones is accompanied with the possible later development of superimposed sericite, alunite, adular.

Other regularities are displayed by argillisites of zeolite-smectite facies. In so far as it does not belong to the acid type, here a definite H₂O content is observed, and in the basic rocks also CO₂, without change in the contained principal rock-forming components (some Na removal is possible). A slight increase of porosity is observed, up to 10-12%. In deposits with intense appearance of zeolitization (Chikoi-Ingodinskoie part of Transbaikalian region)

may be recorded a noticeable Ca addition, for example in the metasomatic Gornoie deposit, nearly double compared to the initial granites. This reflects a specific process, i.e. the absence of a clearly expressed acid leaching.

Parageneses and facies of argillisites. Hydrothermal argillisites. *Quartz-kaolinite facies* is extending in diverse epithermal deposits. It forms under the influence of acid solutions in conditions of small depth and low temperature and is accompanied by antimony-mercury, gold, gold-silver, more rarely fluorite and uranium mineralization. Quartz-kaolinite argillisites characterize insular arcs and continental margin areas and much less often are found in boundary zones of inner tectono-magmatic activation. Typical instances of development of these argillisites are metasomatites of gold-silver deposits of volcanic belts in N-E Russia (Okhotsk-Chukotski belt), in the Transcarpathia (Alpine belt), in northern and southern Cordillera, on the island arcs of the Pacific Ocean, etc. A great part of quartz-kaolinitic argillisites corresponds to the so-called sulfato-acid (high sulfidation, advanced argillization) type of perioric metasomatites formed under the influence of high-acid sulfates and chlorid-sulfatic hydrotherms, principally of magmatic provenance [Heald *et al.*, 1987].

Important minerals of these facies are kaolinite, quartz, chalcedony, alunite, dickite; in different varieties opal, jarosite, mixed-layered minerals (kaolinite-smectite, illite-smectite), sulfur, hematite, iron sulfides, gypsum, baryte. To accessory minerals belong anatase, apatite (and other phosphates), sulfides of arsenic, antimony, mercury etc.

Argillized rock of quartz-kaolinite facies form metasomatic perivenous aureoles, the inner zones of which are replaced by quartz-kaolinite associations. In its most general aspect the column of metasomatic perivenous zoning of this facies has the following aspects (from axial solution-producing fracture to enclosing rock): quartz → quartz + alunite → quartz + alunite + kaolinite → quartz + hydromica → quartz + hydromica (or sericite) → chlorite (or corrensite) → propylitized rocks (albite + chlorite + calcite + sericite). Alunite-containing rocks in some deposits extend to depth of 1.2km, where they are replaced by parageneses with diaspore, pyrophyllite, andalusite, zunyite [Goldfield, Red Mountain, Cerro de Pasco etc.], in other cases zones with reduced alunites. In a quartz-hydromicaceous zone there may develop carbonate of the dolomite-ankerite type in case of increased oxygen fugacity. The latter case may represent transfer from argillized rocks to beresite-like, i.e. essentially represent an example of vertical metasomatic zoning. This phenomenon corresponds to some epithermal gold-silver, antimony-mercury and other deposits. Most often quartz-alunite metasomatites form gently pitching stratiform or lenticular bodies, coinciding with the most superficial hypsometric levels of deposits (fig 23.3).

An example of less sulfidized type of metasomatites is given by the Baleiskoie gold-ore deposit in the Transbaikal region [Rusinov & Rusinova,

1977]. A substantial difference of these metasomatites is the absence of alunite in the composition of silicified rocks, which may be linked also with unstable acidity, and in more reduced conditions with the formation of alterites. The general picture of metasomatic zoning is distinguished by the presence of steeply falling fractures, along which develops a superimposed hydromicatization.

Less acid types of kaolinitic argillisites may be represented also by self-formed carbonate-kaolinitic argillisites, known for the present only in relation with uranium mineralization. This type of argillisites develop on some veinous and stratiform deposits of the Transbaikal region (Olovskoie deposit and part of the deposit of the Streltsovskoie ore field) and in the Ronneburg ore field in Thuringen (Germany). Metasomatites are localised in rocks of different composition. Clayed minerals are represented nearly exclusively by kaolinite, besides which exist in alterites, in various quantities, ferrous carbonates and quartz. Smectites are not displayed in outer zones of argillization aureoles, as far as transformations of feldspars start with their immediate replacement by kaolinites and carbonates without reaction of the smectite zone. As standard instance serves the Olovskoie deposit, where it is possible to follow the consecutive development of these argillisites from superficial unchanging granodiorites (fig 23.4). Metasomatic zoning is nearly not expressed. What draws attention is the significant stability of biotite and potassic feldspar, characteristic is also the replacement of parankerite or ankerite of outer zones by siderite or pistomesite in sectors of more intense study. A monoquartzic inner zone, should it occur, does not exceed in thickness a few centimetres, the quartzic “hat” in the supra-ore zone does not develop. Some complicated zonings are developments of mixed-layered minerals, rectorites and tosudites, in intermediate and inner parts of aureoles. A vertical zoning of metasomatites is not characteristic of the described type of argillisites of kaolinite facies (unlike the sulfide-acid), which may serve as a complementary proof of a possible low activity of sulfur in the process of their formation.

Facies of kaolinite-smectite argillisites are in polymetallic, uranic, fluoritic etc. deposit domains of intracontinental tectono-magmatic activation and continental margins.. Characteristic is the localisation of metasomatites in crystalline volcanic or metamorphic rocks of distinct age in the form of relatively narrow zones (a few metres and up to 10-20 metres), controlled by coarse fracturation and zones of fissuration. Argillisites of the given type extend to domain of development of meso-cenozoic volcanisation, for example Mongolia, Transbaikal region, a series of occidental states USA (Utah, Montana, Colorado), Bolivia, domains of alpine folding of central and Eastern Europe etc. In argillilisites on polymetallic and uranic deposits of western USA [Bonorino, 1959, Tooker, 1964] metasomatic zoning may be represented by the following scheme: 0) unchanging rocks; in most cases this is quartzic monzonite of the

tertiary age; 1) chlorite zone, chlorite + pyrite + carbonate + hematite; 2) montmorillonite zone, montmorillonite with admixture of kaolinite and mixed-layered mineral; 3) kaolinite zone with sericite; 4) sericite with local silicification and ore veinlets.

Sections 2 and 3 conditionally, as far as also kaolinite, and smectite develop usually at the same time and only is noted a constant tendency to the growth of kaolinite content in the centre of the aureole. Potassic micas, judging from their intersecting position, represent a later formation of relatively general zoning.

On Russian territory similar appearance of argillization are known in a row of uranium deposits of the Transbaikal region (deposit of the Mogotchinskoie group, Sigirli deposit). Possibly, close to them are also the periere rocks of some mercury deposits (Nikitovka in the Donetsk basin) etc. [Volostnykh, 1972; Kazitzin, 1979]. A typical example of argillilites with somewhat increased carbonate content is the Mogotchinskoe ore field. Here the ore veins and the aureoles of alterites surrounding them are controlled by steeply dipping fracture zones. The thickness of the argillization zones never exceeds 25-30m. The presence of various xenolites significantly complicates the aureoles' morphology. The outline of the metasomatic zoning is as follows: 0) initial biotite granite; 1) outer zone: quartz, microcline, biotite, smectite, kaolinite, dolomite; 2) intermediate zone: quartz, microcline, kaolinite, smectite, ankerite; 3) inner zone: quartz, kaolinite, now and then microcline.

Hydrothermal genesis of this type of argillilites is undoubted, and their extension (apparently also their genetic link) with mineralization is expressed very clearly, unlike the other facies of the argillilites.

The zeolite-smectite facies includes various metasomatites, which are not wholly locked up in the group of products of acid leaching. In their composition predominate smectites or smectites in parageneses with zeolites. In other minerals may exist kaolinites, celadonites, carbonates, mixed-layered mica-smectites, chlorite-smectites with significant (about 50%) content of swelling inter-foliated layers, berthierites, quartz, fluorite. Apart from contemporary volcanic domains, this facies is also found in some ore deposits of the Mesozoic-Cenozoic age, in uranic deposits and ore-displays of the Transbaikal region, Bulgaria, Chukotski, Tchechskoie massif, polymetallic and sulfidic with native copper of displays in Bulgaria and a few others [Kostrov *et al.*, 1971; Rogova, 1976; Petrossian & Buntikova, 1981; Tchernikov *et al.*, 1983].

The relation of age and genesis of this facies of metasomatites with mineralization is not wholly clear, as far as in many cases hydrothermal transformations have a small extension. Metasomatites sometimes in themselves represent an increased deposit of zeolite and bentonite raw material. In many cases metasomatites coincide with fields of extension of basaltic volcanism or develop in immediate vicinity with them (eastern and southern Mongolia,

Transbaikal region), less typical of their vicinity with dacite-andesite volcanism (Bulgary, Caucasus).

In the composition of facies are distinguishable three subfacies: smectite with calcic zeolites, smectite with celadonite, cristobalite and high silicic Na-K zeolites; and essentially smectites. In connection with the first one is known an uranium deposit of the so-called monometallic β -uranotil type (Transbaikal region, Russia). Subvertical zones of metasomatic transformation have here an extension of a few km and a thickness up to a few tens of meters. Metasomatic minerals are represented nearly exclusively by dolomite and calcic smectites, veinous minerals: desmine, very rarely calcite, quartz; ore minerals: uranotil, in a lesser degree uranophane and autunite, which basically develop in a zone of near-superficial oxidation. The thickness of the ore bodies reaches 10m, but in dipping they reach a depth of 800 m and more (fig.23.5). Ore bodies represent a system of veins of breccia-like deposition, in which fractures of laumontitized granites are cemented by desmine and β -uranotil; moreover the last generation of zeolites developed after the uranium minerals, and calcite ends the process of deposition of vein minerals. Metasomatic zoning in perior rocks is nearly not expressed at all and may be displayed only in increased zeolite (laumontite) content in perifracture zones of maximal alteration.

Another subfacies of metasomatites with a portion of nearly exclusively high-siliceous zeolites of the heulandite group is widely developed in many domains of paleovolcanism, where it occupies an important area, but sometimes contain economic ore mineralization. So, for instance, in the northern part of the Tulukuevskoe caldera (Transbaikal region) in connection with these metasomatites develop pitchblende-coffinite ores with native arsenic (fig. 23.6). Alterations occupy an area of 15-20 km², the entire section of volcanic rocks, 500-600m thick and, partly, early paleozoic granitoids of the basement. The form of ore bodies is stratiform fissured. Zeolites are represented grosso modo by Na-K clinoptilolites and mordenites; moreover the latter fill, basically, sections of veinlets, and smectites are related to high-rank Na or Ca diversities. Ore bodies are surrounded by aureoles of ore-accompanying metasomatic berthieritization, but in the roof are observed Fe-Mg carbonates. Vertical metasomatic zoning is hardly developed, and only at great depths are recorded mixed layered mica-smectite minerals.

Ore-accompanied veinlet-metasomatic transformations in argillites are tightly linked in extension with ore depositions, they often have a metasomatic nature, but can also result from depositing in open cavities and fractures. They develop somewhat later zonal aureoles of argillites, but precede productive ore stages; in other cases they may appear simultaneously with ore minerals or after them. Mineral composition of ore-accompanied metasomatites are relatively simple, they are presented as berthierite, carbonate (principally of iron), adular, mixed-layered minerals, rarely zeolite and fluorite, tossudite etc. Amidst them,

perhaps, the most spread are berthierites, which are particularly characteristic of uranium and gold-silver deposits. The level of this development is always much lower than with argillisites, but the dimensions of the aureoles always exceed those of ore bodies. Metasomatic behaviour is what most characterizes berthierites; moreover it most often forms pseudomorphoses on beforehand kaolinized plagioclase and on biotite. Apart from the variety with 7A structure, sometimes are also found mixed-layered ones. Carbonates form systems of thin veinlets as well as zones of metasomatic carbonatization. Amidst them predominate ferrous or manganous varieties such as siderite-magnesite, siderite-rhodochrosite, and also ankerites. More rarely in contact with ore veins are observed developments of thin edgings and narrow zones of hydromica and mixed-layered mica-smectites. Adular as ore-accompanied mineral is nearly always observed on many gold-silver epithermal deposits in argillisites of the acid type, where they usually also extend to portions of development of gold-sulfidic mineralization.

Deposition of the enumerated minerals submits, on the whole, to a well-known plan of development of processes of acid bleaching and accompanying deposition, when in the composition of ore-accompanying minerals entered components secreted from enclosing rocks. However, there are frequent cases of development of minerals requiring addition of complementary elements. Amongst these, lenticular tossudite may be mentioned. This has been studied in many near-surface, low-temperature deposits of gold, uranium, silver, mercury. Tossudite usually spreads to masses of ore-minerals or fills intersecting post-ore zones of jointing.

Synvolcanic argillisites of the domain of contemporary volcanism. Metasomatites, confined to domains of active contemporary or young Pleistocene-Holocene volcanism, contain a significant quantity of clay minerals, but also a series of other minerals characteristic of low temperature conditions (zeolites, sulphur, opal, etc.).

The character of hydrothermal formation is divided according to the type of thermal waters and in a lesser degree to the composition of the initial enclosing rocks. Amongst studies in present times of thermal waters are clearly enough distinguished three fundamental types [Naboko, 1974; Lebedev, 1975]: 1) low mineralised subneutral, principally chlorid-sodic waters, not linked with concrete volcanic constructions; 2) ultra-acid and acid sulfato-chloridic waters of volcanic apparatuses; 3) highly concentrated carbon dioxide brines of rift domains. Correspondingly, three basic varieties of hydrothermal alteration are distinguished, each of which is characterized by its own specific gathering of mineral parageneses and zoning.

Argillisation, linked to the influence of chlorid-sodic hydrotherms. Alterites in the realm of unloading of thermal waters of a given type occupy a very great area, up to 10.000 km² and more, although the degree of alteration is

most often insignificant or moderate. Display of this type has been studied in many regions of the world and coincide, grosso modo, with the Pacific ocean volcanic ring (New Zealand, Kamchatka, Kurile islands, Indonesia, Japan, Philippines) but also in other regions (Iceland, Italy). Thermal waters are usually characterized by high temperatures, up to 300°C and more (Wairakei, Waiotapu, Mutnovskoie deposit, Los-Azufres, Pauzhetka) and relatively low mineralization, though it may in some cases reach 15-18 gr/l. In salted composition NaCl rarely predominates (2-12 gr/l), Si, K, B concentrations attains hundreds of mg/l, rarely up to 1-2 gr/l, but Ca not more than 200-300 mgr/l, very low usually Mg, Al, Fe contents. The content of silicic acid roughly corresponds to the solubility of quartz at a given temperature. In gas composition CO₂ usually predominates, H₂, N₂ etc. contents are insignificant. Some ion ratio, for instance Na/K, are characteristic, amounting as a rule to 10-12, and only in diluted low-temperature waters, but also in systems with parts of sea water it grows up to 20 and more. Value of pH of waters on the outflow after degazation amounts to 7.2-8.2; however, in the existing conditions of vapour separation acidity of the solutions is significantly higher. So, according to direct pH measurement in borings these values at 140-150°C amount to 5.3-6.5 [Zhdanov *et al.*, 1994]. Consequently, in the influence waters of this type are near-neutral and feebly acid.

Approximately, vertical zoning of hydrothermal alteration may be defined under four zones from above down-wards. The first one forms at the expense of hydroxyen sulphide, it is 0 to 50-60 m thick, its characteristic minerals are kaolinite, opal, alunite; iron hydroxide. The second zone consists substantially of argillilites of zeolite-smectite composition. The third zone is characterized by the development of mixed-layered mica-smectites, chlorite-smectite (transferred, as temperature increases up to 200-300°C, to illites and chlorites), wairakite, calcite, prehnite, quartz, epidote, adular, albite. In lower zones temperature may reach 260°C. The fourth zone is represented by propylitized rocks with chlorite, epidote, albite, adular, calcite, sometimes in the highest-temperature systems with actinolite, andradite, apatite (Mutnovskoie deposit in Kamchatka, Los Azufres, Philippines) [Steiner, 1977; Cathelineau *et al.*, 1989]. Illite here is replaced by mica of phengite or muscovite composition in temperatures between 270 and 310°C.

A few other types of zoning are observed in geothermal systems with sharp predominance in sections of vulcanites of basic composition in Iceland in the hydrothermal systems Hveragerbi, Reikyanes, Hengill [Kristmannsdottir, 1975; Fridleifsson, 1991]. The composition of the hydrotherms, although near that of sea water, differs in its very lower pH value, about 4.5 and much higher content of ore components. Deep boreholes reach nearly 3 km and the vertical metasomatic zoning has the following aspects (from above downwards):

1. Zeolite-smectite zone: mordenite, laumontite, calcite, analcime, nontronite, saponite. The zone is limited in heat to 200°C and in depth to 400-700m.

2. Zone of mixed-layered chlorite-smectites with variants, sometimes with prehnite, calcite; limits: 230-240°C and 800-1200m.

3. Chlorite-epidote zone. Chlorite replaces mixed-layered minerals at about 230-240°C, epidote forms at 260°C ; depth limit : 1700m.

4. Epidote-actinolite zone (actinolite stable at 300°C).

On the whole, for this group of hydrothermal alteration the temperature factor is commanding and shows the greatest influence on the character of mineral transformation. So, for instance, in all geothermal systems are traced the following series of alteration clay minerals (in rising temperature): acid volcanic glass or plagioclase → smectite → mixed-layered mica-smectite → illite → sericite (muscovite); or on basic volcanic glass: nontronite (saponite) → corrensite → chlorite; for zeolites: clinoptilolite → mordenite → laumontite → wairakite.

Hydrothermal alterations, linked with the influence of acid and ultra-acid hydrotherms, belong to the solfataras types, i.e. to such replacements the formation of which is in a high degree distinguished by the presence of sulfate ion. This type may be divided into two groups: the near-surface, substantially sulfatic type and in depth the sulfato-chloridic.

Near-surface argillization appears, grosso modo, as a result of oxidation of hydrogen sulfide in hydrotherms, and may also be observed on slopes of volcanic apparatuses. Water temperature usually does not exceed 100°C, pH is between 1.5 and 4, general mineralization of a few gr. per litre. Thickness of altering rocks oscillates between a few metres and 50-60m. Vertical metasomatic zoning usually has the following aspects (from above downwards): opalites, opalites and alunites, kaolinite with alunite, kaolinite, mixed-layered kaolinite-smectites, illite-smectites, initial rocks. A peculiarity of near-surface hydrothermalites is the wide development of disequilibrated associations and metastable phases, for instance pyrite with marcassite, pyrrhotite and greigite, kaolinite together with metahalloysite, mixed-layered kaolinite-smectite. An important factor of mineral formation is oxidation of hydrogen sulfide and diluted hydrotherms of rain waters.

Deep acid bleaching is characterized by a very great level of appearance. It is conditioned by the influence of ultra-acid sulfato-chlorid waters genetically and spatially linked with volcanic formations, as a rule of the andesite type, situated in a condition of long rest. Temperature of the hydrotherms reach 320°C (in deep parts probably even higher), pH from 0 to 3.5, amongst anions predominate chlore and sulfate-ion, general mineralization reaches 10gr/litre, but in acidest systems with pH near zero, up to 100 gr/litre [Delmelle & Bernard, 1994]. As a rule these displays are characteristic of island arcs. They

are studied in Japan (hydrothermal systems of Otake, Hatchobaru, Matsukawa), and Indonesia (Sumatra, Java), in Taiwan, Philippines, Kurile islands (Kunashir, Paramushir).

A very clear example of development of acid argillites is given by the geothermal systems of the Philippines, in particular the thermal field of Tongonan [Reyes, 1991]. Temperature of acid waters attains 320°C at depths of 2400 m, pH (at outflow) about 4-4.7, chlorine content is 3 to 20 times over that of sulphate-ion, general mineralization amounts to 11 gr/l. Metasomatites are concentrated exclusively along steeply falling zones of explosive fracture, their thickness usually does not exceed a few tens of metres, but lateral zoning has not been sufficiently studied. The basic motif of vertical zoning is represented by the following zones, from above downwards:

1. kaolinite + alunite + sulfur +pyrite (up to 120°C)
2. dickite +kaolinite +alunite +anhydrite (120-200°C)
3. dickite + pyrophyllite (200-250°C)
4. pyrophyllite + illite (230-320°C)

In surface parts of the section, moreover, may exist opal, trydimite, cristobalite, but in great depth in acid metasomatites exist zones of germinal greisenization, characterized by the presence of topaz, lazurite, tourmaline, zunyite, fluorite, muscovite. Everywhere zones of acid metasomatites prove much later than argillites of the subneutral type (fig 23.7).

The question of the source of acid and ultra-acid hydrotherms is not fully resolved, and some authors prefer a meteoric genesis of those waters as a result of sulfur oxidation. But, considering the geological conditions of the thermal manifestation of such a type, their coincidence with determined geodynamic realms, high content of sulfur, chlorine and fluorine in the thermal waters, the deep character of development of metasomatic transformations, all prove their magmatic genesis. Like one of their possible variants, a likely process is the formation of juvenile magmatic gases in meteoric waters of a mud of stratiform fissural type. The observed vertical and lateral zoning of metasomatic alteration coincides in a high degree to the metasomatic zoning in epithermal deposits of the acid-sulfatic type (advanced argillization).

Hydrothermal transformations linked with influence of heated brines. This type of alteration is linked with contemporary rift systems and coincides (but not always) with volcanic or intrusive formations. It is linked to high-temperature carbon dioxide brines of the geothermal fields of Salton-Sea (California), Cerro-Prieto (Mexico) and other great copper displays in the limits of the rift zone of the Californian gulf, apparently also in their vicinity the brines of the Cheleken peninsula (Turkmenia), the graben of the red sea, etc. In the latter no hydrothermal transformations have been noted, and there is no link with magmatic display. Specific thermal waters exist in high general mineralization (up to 260-280gr/l) and often in high contents of carbon dioxide (up to a few

gr/l). Temperatures of boiling brine in deposits of the Californian rift attain 350-390°C. Enclosing rocks are here represented by delta-shaped facies of sedimentary rocks. On the territory of thermodisplay of Salton-Sea are formed five young rhyolitic and slag cupolas, the age of which amounts to 10-16 thousand years. These extrusions are often covered by sediments, but in three of them occurs a gas secretion (mainly CO₂) and vapour-water blends from cracks, tracing coarser lineaments of the north-western course [Muffler & White, 1969]. It is not excluded, however, that the main source of heat in these systems be linked with concrete magmatic displays, but with deeper processes, conditioning the formation of “young oceans”, in which also occur rifts of the Californian gulf, the Red sea and other regions.

Although the depth of drilled boreholes attains 4.5 km, maximal temperatures are recorded in various records. Thermal waters are basically potassic-calcic-sodic chloridic with high content of ore-components; the carbon dioxide content attains 96% in gaseous phase and 5 g/l in brine; the value of pH at 25°C is 4.6-5.5.

Hydrothermal alterations occupy an area up to tens of km² and are controlled by permeable zones and warming up fractures. Vertical metasomatic zoning is very similar to one type of subneutral transformation in volcanic realms. The main difference is the full absence of new formations of zeolite and the very insignificant development of feldspars, adular and albite (fig.23.8).

Conditions of argillite formation. Evaluation of the condition of argillite formation is complicated by the absence of reliable thermodynamic constants for smectites, zeolites, berthierites, and also insufficient experimental research in low temperature realms. Nevertheless, some conclusions may be drawn.

Kaolinitic argillites undoubtedly present a facies of maximal acidity and have an obvious analogue amongst solfataral argillites of superficial as well as deep type. Judging from the high extension of quartz-kaolinite association with alunites, the influence of hydrotherms may have a sulfatic or chlorido-sulfatic character with pH at 4 and less. There may be some difference only in the carbonate-kaolinitic variety of these argillites, which corresponds to conditions of greater CO₂ fugacity. The relatively feeble similarity in the composition of altering rocks of calcic hydromicas and mixed layered illite-smectites indicates a (basically) non-high temperature of the process: about 250°C. A reaction zone of smectites in contact with enclosing rocks will not develop in all cases, which may be conditioned by the proximity of kinetic factors causing “vanishing zones” in an infiltration metasomatic column. This phenomenon was predicted by D.S.Korzhinsky but later theoretically and experimentally studied by V.N.Balashov and P.Ch.Lichtner [1994].

A smectite-kaolinite facies of argillites corresponds to conditions of moderate acidity, but the temperature conditions, probably, were close to the

preceding facies. This permits to indicate the frequent presence of carbonates with very feeble development of a quartz core, and relatively rare occurrence, in the composition of intermediate zones of metasomatic columns, of illite-smectite mixed-layered minerals. The latter was only possible at temperatures not above 180-200°C, as far as at its further growth smectites were on the whole replaced by hydromicas and sericite.

As regards smectite and zeolite-smectite metasomatites, they are not characteristic of acid conditions. These metasomatites have a few analogues in the realms of unloading of thermal waters, which permits to determine the conditions of their formation at low temperature (~130-150°C and lower) and near-neutrality. According to data of A.V.Zotov, direct pH measurement in high-temperature boreholes [Zhdanov *et al.*, 1994] points to the fact that these parageneses are stable in near neutral or even feebly acid milieu with water pH about 6 at 140-160° C. Extrapolation of these data in high temperature realms reveals some replacement of a realm of smectite stability by a one of more acid value, as, at 180-200°C water pH must correspond roundly to 5. Laumontite, so widely spread in the metasomatites of the central Transbaikal region, also characterizes a completely determined temperature range, from 120 to 200°C [Fridleifsson, 1991] with near neutrality of the solutions. At the highest temperature calcic zeolite, wairakite are perfectly uncharacteristic of ore deposits, though usual enough in high-temperature boreholes of contemporary thermodisplays.

Ore-accompanying metasomatites, chlorite, berthierites, carbonates, hydromicas, adulars, etc. may arise as a result of the boiling of solutions [Naboko,1974] as factor of pH increase. The possibility of sharp pH growth of thermal waters, under the influence of a part of CO₂ was theoretically mentioned on the example of the Broadlands deposit in New Zealand, relatively rich in carbon dioxide [Browne & Ellis,1970]. It was shown that at the decrease of carbon dioxide content to 0.15 m its loss to 0.03 at decontamination causes a pH increase to 0.6-1.2 units, but this value does not prove certainly significant for a sharp change of acid-alkaline condition; therefore in the given cases may be applied a model of biphasic gas-liquid system [White *et al.*,1971], providing for inflow of saturated metals of the brines after stage of acid bleaching.

Fig.23.9 presents an outline of spreading of different facies of argillites in dependence upon temperature and acidity. It has a qualitative character, inasmuch as deposition of minerals in equilibrium, of course, depends also in a significant degree upon the concentration of the corresponding components. For some of them the influence of the temperature factor and acidity has a much greater importance, which also permits to utilize such a kind of formation for a rough estimate of the physico-chemical condition of argillization. The remaining equilibriums are plotted, starting from available experimental and calculated data, and so also are observed in realms of contemporary mineral formation.

In acid conditions the boundary conditions of argillization are determined by kaolinite = pyrophyllite equilibrium, which according to numerous experimental data, corresponds to a temperature of about 290°C. Alunite in low-temperature conditions corresponds with a very acid condition of the milieu, as at 90°C pH should not exceed 2.5 and at 200-300°C it is situated between 2 and 3, since with growth of alkalinity may occur the reaction of alunite + quartz + H₂O = dickite (kaolinite) + K⁺ + 4SO₄²⁻ + 6H⁺ [Zotov, 1967; Hemley *et al.*, 1969; Inoue & Utada, 1991].

In subalkaline conditions the temperature limit of argillites roughly corresponds to 190°C, determined by the stability of analcime [Matthews, 1980]. This reaction is usually utilized to mark the boundaries of the zeolite facies of metamorphism. In the field of hydromicas and mixed-layered mica-smectites the limit between formation of beresites and argillites, apparently, may lead somewhere to a level of development with content of swelling stratas not above 20%, i.e. at a temperature roundly of 230-250°C.

Argillization and processes of ore-formation. Argillites are characterized by multiform low-temperature mineralization of gold, uranium, fluorite, antimony, mercury, arsenic, silver, zeolite, bentonite. However, a multiform deposit unique as to reserves does not characterize them. Practically every display of ore mineralization in argillites is related to the deposit type, when formation of metasomatites and ore bodies is divided in some time intervals. Excluded are only deposits of zeolites and bentonite raw material, which in themselves represent metasomatic rocks. As with other metasomatic low-temperature types, ore veins and zones of disseminated mineralization only sometimes coincide with a portion of maximal bleaching, in general they extend arbitrarily in relation to the zoning, although in unaltered rocks they sometimes do not grow.

Ore content of argillites depends upon their facies belonging as well as the geotectonic conditions of their display. Interrelation between degrees of ore-content of argillites with their geotectonic (geodynamic) position and the facies varieties of hydrothermal alterations are shown on table 23.1. The degree of ore-content of argillites is very strongly diverse. So, in wide fields of argillized rocks of island arc domains of active volcanization it occurs at considerable depth intervals, basically from a few centimetres to a few decametres, i.e. in portions with maximal display of gradient of outer condition. The thickness of ore veinlets is insignificant, the concentration of metals is very low and with rare exceptions they are not comparable with hydrothermal ore deposits. Basically, totally oreless and oceanic apobasaltic argillites, to the exclusion of those that belong to the sulfide formation of the “black-smokers”.

Argillites of the acid type (quartz-kaolinite facies) are widely spread in connection with antimony-arsenic-mercury, gold, gold-silvery deposits and displays, especially in realms of continental outskirts (western USA, north –

eastern Russia, low Amur area, Andes, etc.). The amount of mineralization may be totally insignificant. To kaolinite-smectite argillisites found in slightly acid milieu, correspond a wide spectrum of useful material either of ores (of uranium, arsenic, polymetals) or oreless (fluorite). However, coarse deposits connected with metasomatites of this type are unknown, except some deposits of fluorite. Zeolite-smectite argillisites, as remarked above, either by themselves represent deposits of sorbtive materials, or contain small deposits of uranium ore.

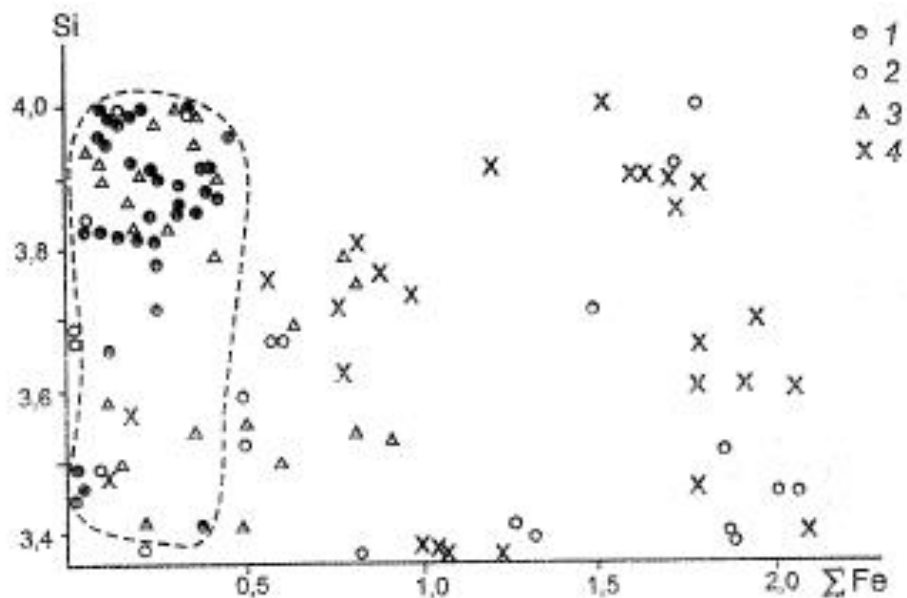


Fig. 23.1. Contents of silica and iron in dioctahedral smectites.

Field of hydrothermal smectites limited by dotted line: 1—figurative points of hydrothermal montmorillonites and beidellites; 2—dioctahedral smectites of the crust weathering; 3—sedimentary smectites; 4—smectites of altered oceanic basalts [Dritz & Kossovskaya, 1980, 1990; collective data].

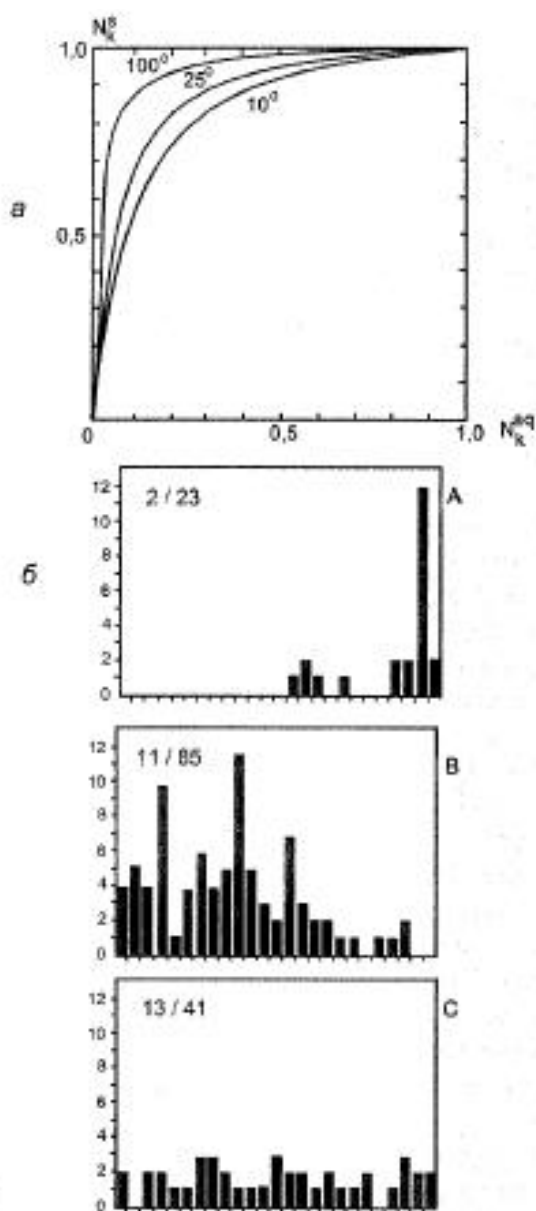


Fig. 23.2. Dependence of content of potassium in alunites on temperatures.

a – isotherms of ideal distribution of potassium between alunite and solution, calculated at 10, 25 and 100°C [Zotov, 1971]; *b* – histograms of distribution of content of potassium and sodium in alunites of various genesis [Stoffregen, 1990]; in left upper corner, number of locations of alunite and general number of analyzed samples; A – alunites from pyrophyllite-containing metamorphic samples; B – alunites from hydrothermal ore deposits; C – hypogene alunites (diagenesis and weathering crusts).

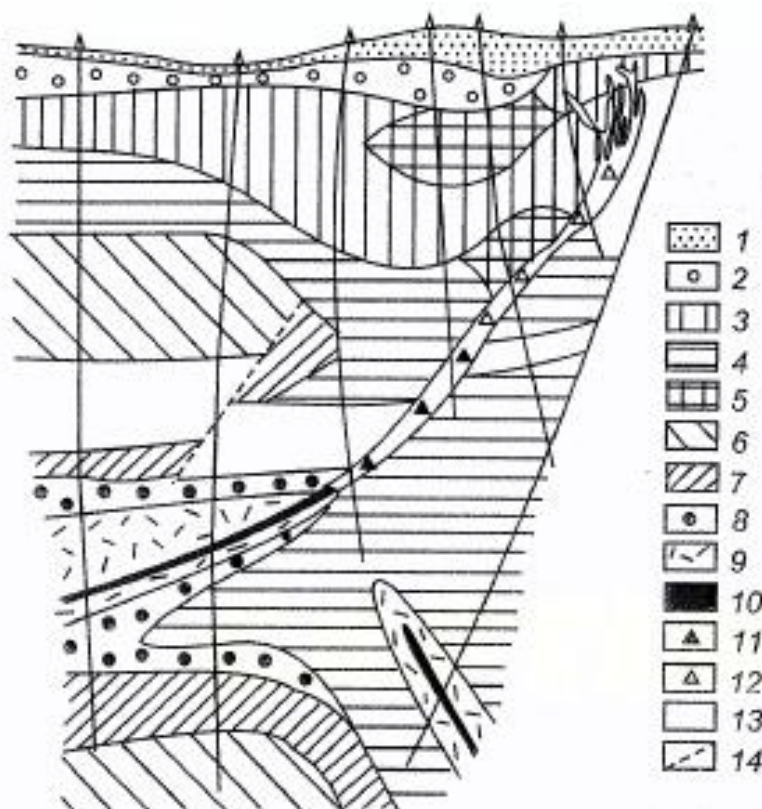


Fig. 23.3. Schematic geological cross-section of altered tufas of polymetallic deposits of Beganskoie [Volostnykh, 1972].

1-slope waste; 2-9 zones of altered rocks; 2- monoquartzites; 3-silicified rocks with alunites; 4-kaolinites and silicified rocks; 5-silicified, kaolinized and alunitized rocks; 6-montmorillonitized; 7-kaolinite-chloritic; 8-kaolinite-hydromicaceous; 9-hydromicaceous-chloritic; 10-12-veins: 10-polymetallic, 11-baryte-polymetallic, 12-barytic, 13-sedimentary argillites, 14 - dislocation breaks.

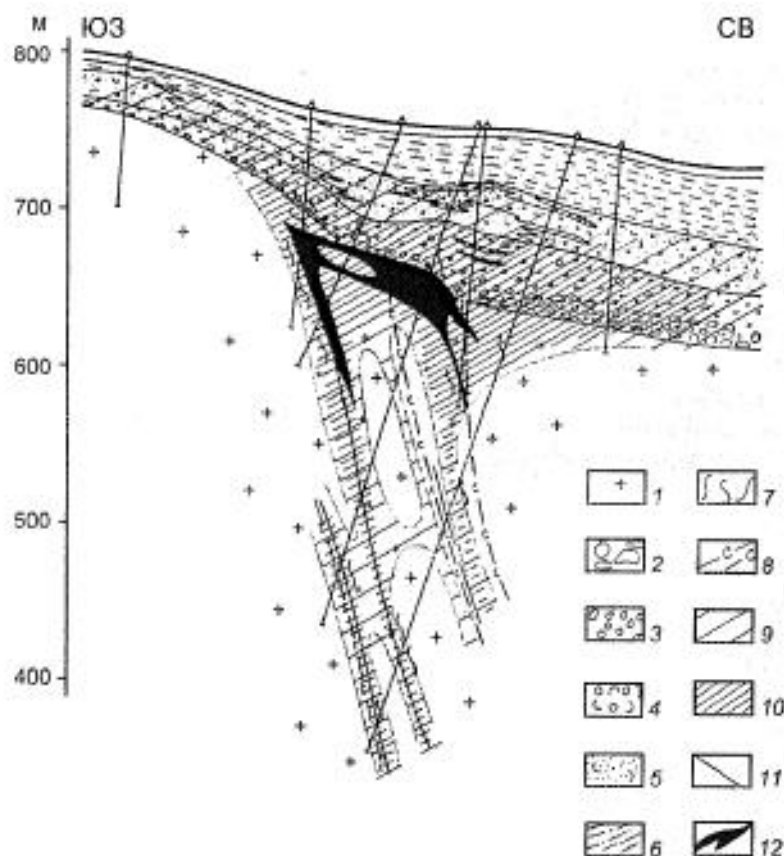


Fig. 23.4. Development of carbonate-containing kaolinitic argillisites on uranium deposit of Olov (East Zabaikal), schematic geological cross-section (after V.A.Golovine).

1–granodiorites of the Orlov complex ($J_{2,3}$); 2–3–rubbly and coarse-pebbled conglomerates and gritstone; 4–sandstone; 5–tufas and tufo-sandstones; 6–aleurolites; 7–zones of development of recent smectite; 8–greisenized granites; 9–10–weak and intense manifestations of argillized carbonato-kaolinitic composition; 11–fractures; 12–ore bodies.

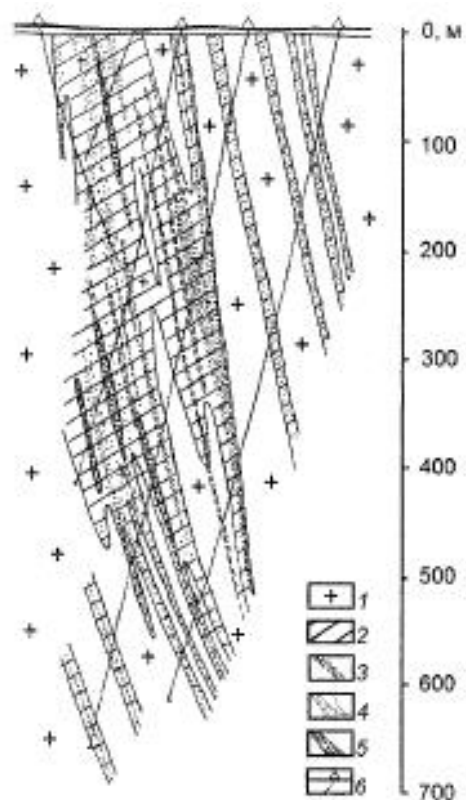


Fig. 23.5. Schematic geological cross-section through Gor deposit (on materials of V.P.Rogov, V.I.Melnikov, V.V.Davydov and collective data).

1–granites (J₃); 2–zones of smectitization; 3–area of development of veinlet desmine;
4–zones of laumontitization; 5–ore bodies; 6–holes.

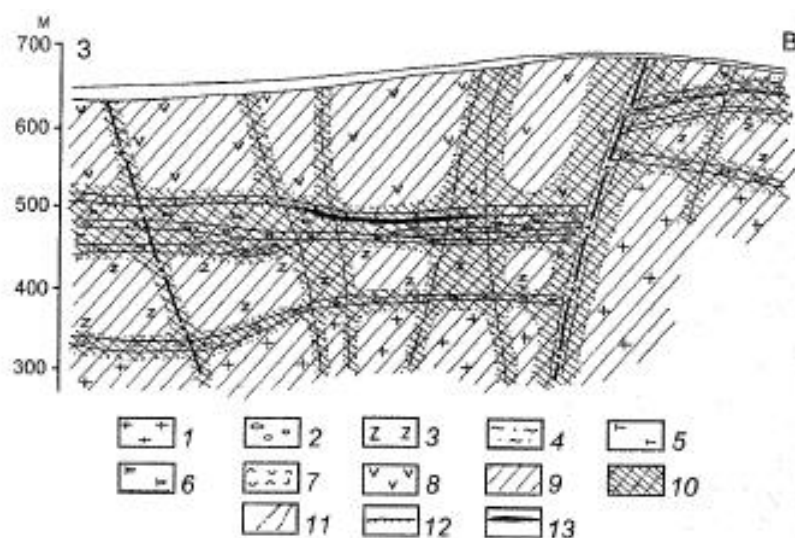


Fig. 23.6. Schematic geological cross-section through the Dal uranium deposit (East Transbaikial).

1-early Paleozoic granitoids; 2-conglomerates; 3-trachydacites and their ignimbrites; 4-lava breccias; 5-basalts; 6-andesites and andesito-basalts; 7-tufas; 8-rhyolites and rhyolitic ignimbrites; 9-portions of development of weak or moderate smectitization; 10-intense development of smectites and zeolites along dislocation breaks; 11-fractures; 12-gentle fractures; 13-ore bodies.

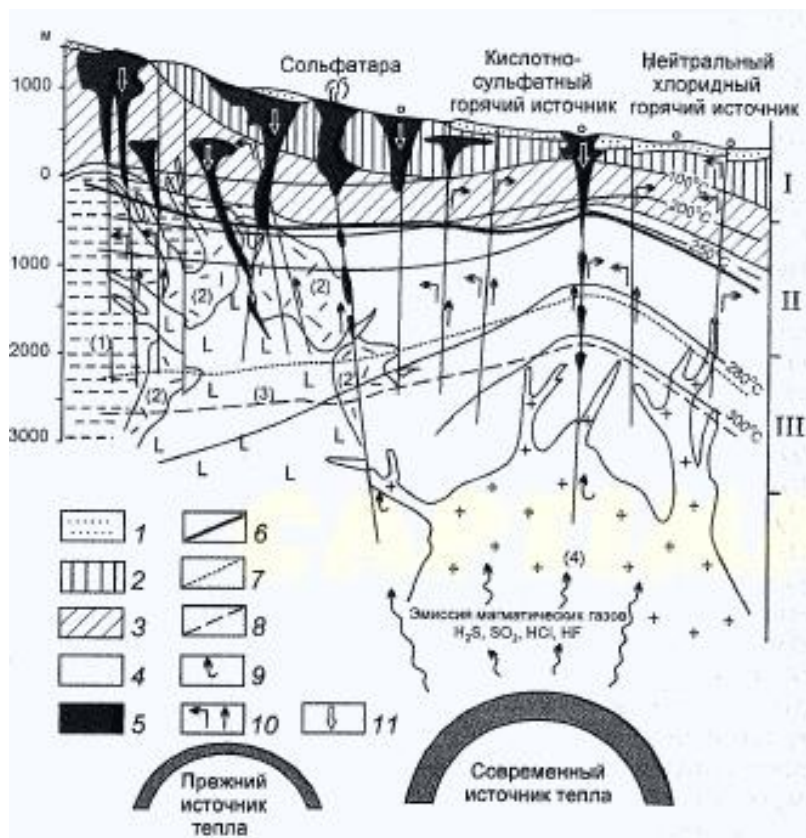


Fig. 23.7. Character of development of argillites of ultra-acid type in the hydrothermal system of Tongonan (Philippines) [Reyes, 1991].

1–unaltered rocks; 2–smectite zone; 3–transitory zone; 4–illite zone; 5–transformations of acid type; 6–limites of appearance of epidote; 7–limit of appearance of biotite; 8–limit of appearance of amphibole; 9–flows of deep acid fluids; 10–flows of subneutral chloridic waters; 11–sulfatic reversed flows (influx).

(1), (2), (3), (4)–successive phases of introduction of intrusive bodies from late miocene to pleistocene; I–late pleistocene and contemporary lava flows and volcanoclasts; II–late pliocene and early pleistocene hyaloclastites; III–late miocene limestones, aleurolites, sand sedimentary breccias.

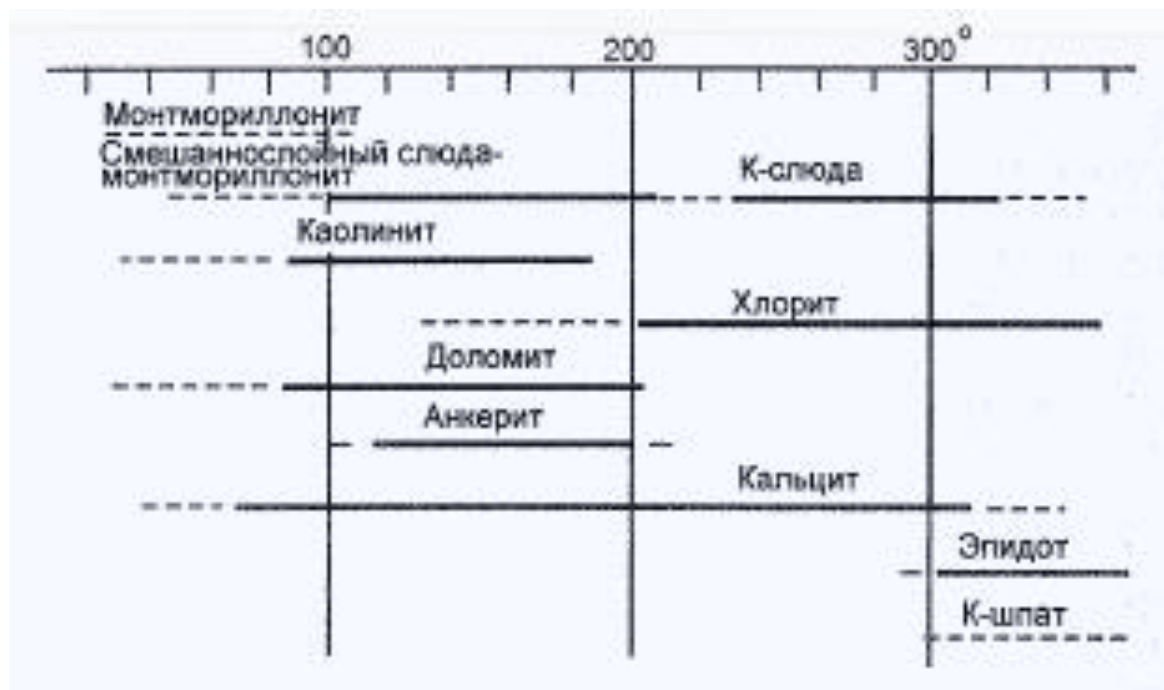


Fig. 23.8. Dependence of extension of hydrothermal minerals upon temperature in the geothermal system of Salton-Sea [Muffler and White, 1969].

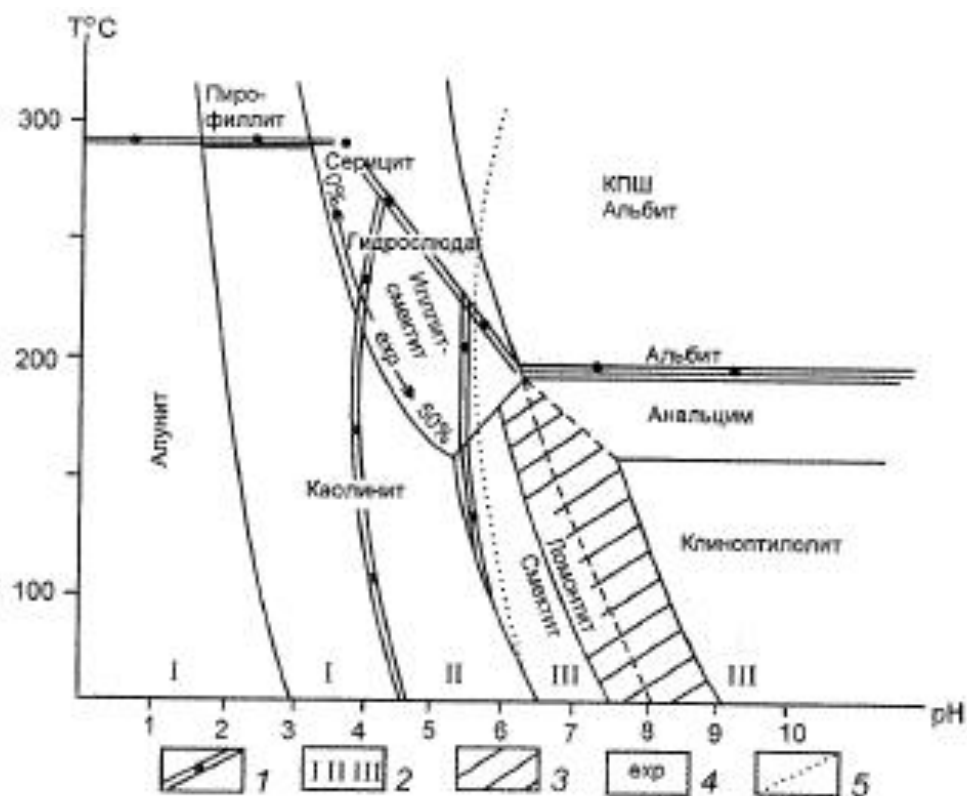


Fig. 23.9. Dependence of extension of argillites of various facies upon temperature and acidity.

1—limits of field of argillites of various facies of acidity; 2—field of argillites: I—acid facies (kaolinite, alunite-kaolinite argillites), II—field of argillites of kaolinite-smectite facies, III—field of smectites and zeolite-smectite argillites; 3—area of newly distributed transition of smectite-zeolites; 4—quantitatively swelling interlayers in mixed-layered mica-smectites; 5—neutral pH value of water; exr — mixed-layered mineral of mica-smectitic type with content of swelling layers not higher than 50%.

CHAPTER 24

Metasomatic rocks of shear zones and deep fracture zones

Carbonated metasomatites. The products of carbon metasomatism are recorded in many groups of ore fields [Tomson *et al.*, 1989] although the question of the origin of carbon matter in them is still in discussion. The term “carbonated metasomatism” was introduced by P.F.Ivankine [Ivankine & Nazarova, 1984], who meant by it a process of deposition of carbon matter (CM) in the aspect of graphite or various carbon combinations in terrigenous detrital rocks. At the beginning, CM in such rocks was counted as organogene, transformed and redeposited in a process of diagenesis and regional metamorphism. It became apparent, however, that a definite part of terrigenous masses was carbon enriched coinciding to zones of important faults or regional shear zones. Beside the fault CM decreases, as was observed in a black-schist mass in Primoriei [Tomson *et al.*, 1989]. In the region of the gold ore deposit of Muruntau in Uzbekistan, CM enriches the mineralized series of the “mottled bessapane” in the limits of the ore field. In these this mass contains practically no CM and presents muscovite-chlorite schists. Examples were observed of not very distinct structures of replacement of silicate grains by CM, but in most cases CM is distributed in intergranular extensions or fills small cracks in the rocks. These signs permit to surmise a penetration of at least part of the carbon in the rocks by solutions (or gases) and abiotic CM deposition. Complementary arguments for the use of the endogene origin of the CM are the mass of different black-schist-enriched metals, amongst which are elements of the platinum group, noble metals, rare-earth elements and also the diffusion of CM spread in pyrite fields in volcanic masses. Discussing the problem of “black schists” formation is linked with the absence of reliable signs of metasomatism such as metasomatic zoning and decreasing number of minerals in an increasingly intense process, and also in the difficulty of observing distinct structural signs of replacement and studying undetermined paragenetic relations of CM with mineral rocks.

Carbon matter is associated in black-schists masses with pyrrhotite, pyrite, arsenopyrite, carbonates, sericite, ilmenite, albite and quartz. As constantly associated accessories are present native metals (aluminium, tin, copper, lead, zinc). It remains unclear whether these associations are paragenetic or in them are mingled products of various processes.

As examples of display of carbon metasomatism serve the black-schist masses in uranium or gold ore fields of Soukhoi Log in Siberia, Muruntau in Uzbekistan, Stillwater in Canada, Schungite in Karelia. As mechanism of CM deposition from endogene flows are proposed 1) oxidation of CM of reduced deep fluid to carbon (graphite); 2) reaction of disproportion activated as far as the decrease of the fluid temperature, for instance,



3) deposition of paragenesis graphite + sericite as a result of compression of the flow and increase of its acidity [Koltsov, 1995]. In any case the process is linked with the occurrence of reduced deep fluids in a relatively high level of the earth crust. Deep display of CM metasomatism is estimated at a few kilometres.

Black-schist masses include not only disseminated sprinkling of metals, but also coarse deposition of uranium and gold. In the last years came to light a perspective of black schist masses on revelation of industrial accumulation of platinum and metals of the platinum group [Laverov *et al.*, 1997]. Deposition of noble metals and other ore mineralization on products of carbon metasomatism represent an intense pre-ore biotitization (“corneification”) and feeble display of acid metasomatism. It is supposed that an increased background of metals in black schists forms at stages of sedimentogenesis or diagenesis, and as a result of much later hydrothermal processes occurs a redeposition of metals in concentrated form, but a reliable time of introduction of carbon and metals in the sediments has not been established. The majority of researchers think that with any of the enumerated variants this introduction is linked with that of an endogene fluid along important faults of deep origin.

Albitites in zones of fractures of Precambrian shields. High temperature metasomatic rocks, chiefly albite, are spread in Precambrian shields. They have been studied in greatest detail in shields of Ukraine, Aldan and Canada. They are characterized by a pronounced alkaline paragenesis of the inner zone of a column of metasomatic zoning (albite + aegyrine + riebeckite), localized in zones of deep long active faults and great extension either in breadth (from 100 m to a few km) or in length (up to 3 km), with a thickness of a few decametres.

As a result of studying albitites of the Ukrainian shield I.P.Shcherban [1996] distinguished four chief groups of these rock according to the metallogeny: apogranitic, apogneisic, apojaspilitic and linked with carbonatite assemblages.

Apogranitic albitites form lenses in places of conjugate regional submeridional fault with the system of feathering structures. To metasomatism

are subject rocks of an ultrametamorphic assemblage: biotite-quartz-plagioclasic gneisses and biotite-quartz-microcline-plagioclasic granites.

Metasomatic zoning on them has the following aspects (fig.24.1): 0) unaltered granite (microcline + plagioclase + quartz + biotite); 1) microcline + albite + quartz + chlorite + epidote; 2) microcline + albite + quartz + riebeckite + chlorite; 3) albite + riebeckite + aegyrine.

Columns are observed in which riebeckite is lacking in inner zone, and biminerall paragenesis of albite + aegyrine is stable.

Such a zoning permits to predict a high oxygen fugacity and sodium activity and extreme inertia of aluminium and ferric oxide amidst rock-forming components. High alkalinity of the albitizing solution is emphasized by dissolution of quartz in inner zones of the columns.

Apogreisen albitites are principally not distinguished from apogranitic, except that in the inner zone there exists, at places, phlogopite.

Apojaspilitic alkaline metasomatites have been studied in the Belozersk iron-ore region of the Ukrainian shield [Shcherban, 1996]. I.P. Shcherban describes them under the name of “apojaspilitic albitites”, but the rocks do not contain albite and it is therefore expedient to call them aegyrine-biotitic or simply alkaline metasomatites. Below is distinguished the zoning of metasomatites of this type: 0) unaltered rock (quartz + magnetite + carbonate + chlorite); 1) quartz + magnetite + carbonate + riebeckite + chlorite; 2) carbonate + riebeckite + quartz + magnetite; 3) riebeckite + aegyrine + quartz + magnetite. Excess of quartz in initial ferrous quartzites brings about in this case inert silica up to the inner zones, unlike in the apogranitic column. For the rest the tendencies are similar: the process occurring with growth of sodium activity and of bi- and monomineral zones may be explained either by a less intense process [Shcherban, 1996] or, more plausibly, by local occurrence of parageneses of the inner zone under the aspect of isolated nests and lenses amongst isolated innerer zones.

Albitites linked with linear bodies of carbonatites occupy thin (a few meter) margins around carbonatites. In these cases a succession of processes from early to late includes fenitization at magmatic stage, followed by postmagmatic transformation of carbonatites and albitization. The latter is superimposed either on fenites or on rock containing a carbonatite assemblage.

Albitites linked with microcline metasomatites are observed in the north-western part of the Ukrainian shield in a strip of deep faults. Along these faults occurs a wide granitization. Albitization is here related to much earlier (after microclinization) postmagmatic processes, it immediately follows granitization and is accompanied by beryllium mineralization.

Mineralization in albitites of diverse type is represented in basic uranium mineralization, apart from beryllium-bearing microcline-albite assemblages. In the total of signs amongst albitites in zones of faults in the limits of crystal

shields are distinguished three metallogenic types [Shcherban, 1996]: 1) periveinous albites of uranium deposits (apogranitic, apogneisic and apojaspilitic); 2) albitites, accompanied with carbonates with rare-metal mineralization; 3) albitites of beryllium deposits, associated with microcline metasomatites.

Albitites in gold ore fields. Gold mineralization is often accompanied with local occurrence of periveinous albitization. As a result albitic veinlets are produced, to which coincides a realm of increased gold content (for instance in the Muruntau deposit), albite fringing around ore veinlets and veins and bodies of lenticular form in ore fields. A.F.Korobeinikov studied ore bearing of albite metasomatites in the Transbaikal region and in Kuznetsk Alatau. Metasomatites represented in zones composed of albite + quartz + actinolite (albite up to 50-80% vl.) are developed on plagiodiorites [Korobeinikov & Shubin, 1969]. In the outer zone are added to these minerals epidote, sphene and apatite. The determined temperature of albitization varies from 630°C at the beginning of the process to 300°C at the end. The temperature of formation of gold ore veinlets (quartz + sulphides + gold) from a chlorid sodic solution amounts to 360-250°C. In the gold-silver deposit of Tayoltita (Mexico) are described feldspar dykes crossing volcanites and coinciding with ore bodies [Randall, 1968]. Dykes are built of albite, sometimes with admixing of epidote and chlorite. Thickness up to 10 m, extension in breadth and length, 50 m, age is considered as preore. Immediately along the boundary of ore bodies are developed metasomatic albite edgings relieved with removal from ore bodies of epidotization which is transferred into propylitized enclosing rocks.

Phlogopite and biotite veins. In Bulgaria was described an uncommon type of phlogopite rocks [Kotov *et al.*, 1986]. They contain ore bodies up to 1-2 m thick, traced in dip to a few decametres and in length to 100-200 m. This consists practically of monomineral phlogopite rocks with addition of apatite, orthoclase and carbonates. In exocontacts were not noticed substantial alterations of enclosing rocks. Veins coincided with a zone of deep fault; the authors surmise their hydrothermal origin, but a plausible genesis of these phlogopitic rocks has not been established.

In some degree analogous to them are *tabashki* (dykes of biotite-feldspar composition) in the Berezovsk and Kotchkar ore fields of central Ural. Around such dykes, however, is observed biotitization of enclosing granites and border biotite around crystals of microcline. One surmises the metasomatic character of the biotization in these dykes. *Tabashki* were formed after deposition of poor gold ore [Borodaevsky & Cheremisov, 1981] and with the process of biotitization is linked a redeposition of gold and formation of parts of rich ores.

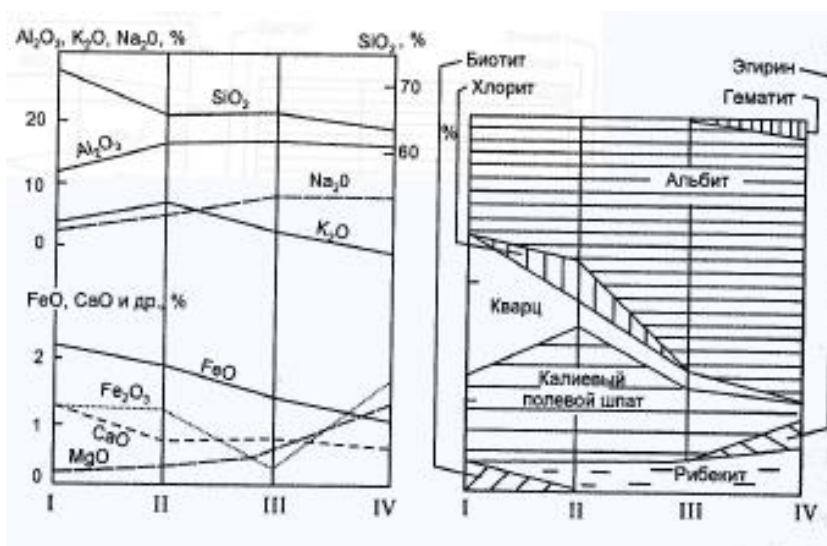


Fig. 24.1. Change of chemical mineral compositions of granites of albitization [Shcherban, 1996].

Succinct glossary of metasomatic terms and synonyms

Zodites [Spiridonov, 1991] are synonyms of listvenites. Their specific property is the presence of chrome-beydellite and chrome-dickite in listvenite parageneses. They are displayed in the Zod gold ore deposit of Armenia.

Quartz-feldspar metasomatites are metasomatic endocontact transformations at early postmagmatic stage in hypabyssal and subvolcanic granitoid massifs. They are found in diverse geological environments : in rare-metal and polymetallic skarns, in copper-molybdenum porphyries, in rare-metal greisens and in some gold deposits. Their composition is quartz + K-feldspar + albite. They precede skarns, greisens and quartz-sericite metasomatites. It is also employed for some metasomatites of fracture zones which may lead to confusion in questions of genesis.

Silica-alkaline metasomatism (K-Si metasomatism) is a collective term designating processes of transformation, basically of quartz-feldspar metasomatites of various genesis. In american literature it is mentioned in relation to quartz-sericite rocks and products of « advanced argillization », which is inexact since such rocks are the result of acid metasomatism (though

potassium content in the rocks may grow, but its activity in the solution is below the stability of feldspars).

Mantle metasomatism is a process of local change of chemical and mineral composition of mantle matter under the influence of rising flow of deep fluids. Strictly speaking, the process is not metasomatic, but rather metamagmatic, since it presents itself as interaction of fluid and magma. Products of mantle metasomatism have been studied in xenolithes corresponding to the assumed composition of mantle matter.

Oksetalites [Kazitsyn, 1970] is a term designating a combination of facies : orthoclase, carbonate, sericite, turmaline and albite. The term did not prevail and is hardly used in the literature.

Advanced argillization (advanced argillic alteration) is a low temperature metasomatism with replacement of initial rocks by quartz with kaolinite and hydromica, sometimes with alunite (of the acid sulfatic type).

Rare-metal alkaline quartz-albite-microcline metasomatites (qualmites) [Kudrine, 1978] is synonym to alkaline metasomatites (potash feldspars and albitites) in fracture zones of crystalline shields.

Phyllisites (phyllitic alteration) are quartz-sericite metasomatites in copper-molybdenum porphyries. Hardly used in russian.

Fragmentary metasomatism [Tsarev, 1984] designates a process of selective metasomatism, in which replacement occurs on a net of fractures. Remaining blocks of unchanching rocks resulting from replacement acquire a rounded form, similar to a pebble in conglomerates. Such rocks often are described as tectonic breccias from the morphological similarity.

Zwitter [Kovalenko & al.,1974] are greisens in which mica is present as zinnwaldite. They contain mineralizations of tin, tungsten, more rarely of tantalium and niobium.

Sharoitization [Biriukov & Berdnikov, 1992] is a process of alkaline metasomatism, in which surrounding metamorphic rocks are replaced by a fine-fibrous alkaline amphibole (sharoite), discovered by V.P.Rogov and appearing as prized stones. Until now only one region of occurrence is known, the basin of the

river Shara in the Baikal region from which come the names of the mineral and the process.

REFERENCES

Note from translators:

АН СССР = Академия Наук Союза Советских Социалистических Республик
AS URSS = Academy of Sciences of the Union of the Sovietic Socialist Republics

АН КазССР = Академия Наук Казахской Советской Социалистической Республики
AS RSSKaz = Academy of Sciences of the Sovietic Socialist Republic of Kazakhstan

АН УзССР = Академия Наук Узбекской Советской Социалистической Республики
AS RSSOuz = Academy of Sciences of the Sovietic Socialist Republic of Ouzbekistan

АН АрмССР = Академия Наук Армянской Советской Социалистической Республики
AS RSSArm = Academy of Sciences of the Sovietic Socialist Republic of Armenia

РАН = Российская Академия Наук
ASR = Academy of Sciences of Russia

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